

ADVANCES IN CATALYSIS
AND RELATED SUBJECTS

VOLUME I



ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME I

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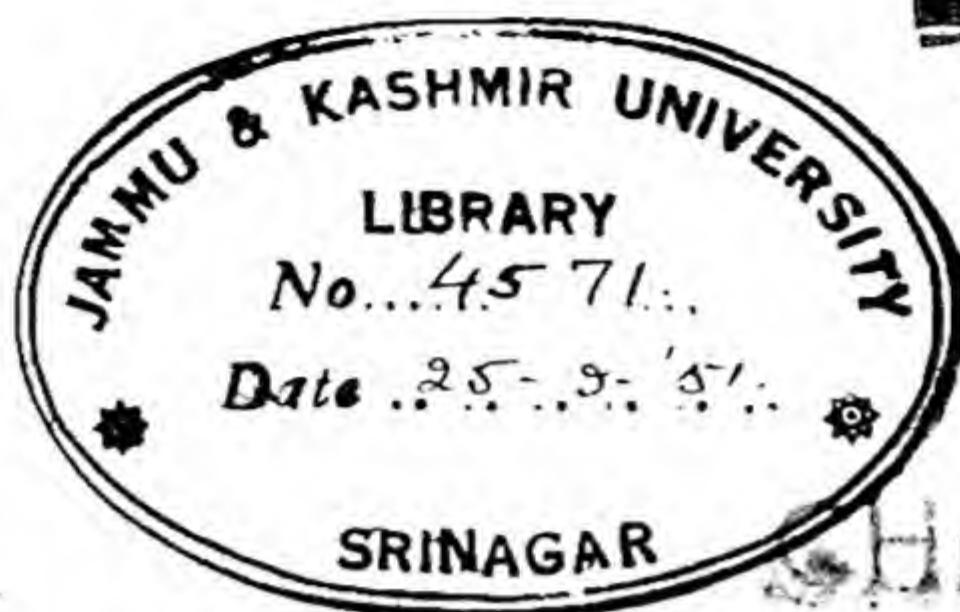
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PREFACE

The use of heterogeneous catalysts as a tool in the laboratory, in preparative chemistry, and in large scale industrial production has expanded beyond any expectations during the last three decades.

Catalytic processes today dominate the production of sulfuric acid, ammonia, methanol, and many other industrial products. The cracking of mineral oils, the hydrogenation, transformation, and synthesis of hydrocarbons are almost all centered around catalytic conversions carried out with many different catalysts including some of highly specific action. Many more catalyzed reactions are being carried out in batch processes and in continuous operations, in heterogeneous and in homogeneous systems.

Similarly, catalysis is being used to an ever increasing extent for the production and transformation of individual organic compounds, a development which started with the catalytic hydrogenation of vegetable oils and fats and which led to the acceptance and daily use of catalytic methods in the pharmaceutical and related industries.

Parallel to this development, the study of natural processes in living matter has revealed the existence and the powerful selective action of an almost infinite number of biocatalysts of highly complicated chemical structures.

In spite of these amazing practical successes of catalytic methods, and of our increasing knowledge of biocatalysts, only modest progress has been made in the scientific elucidation of the working mechanism and of the basic nature of catalytic action. As a consequence, a purely empirical approach is still the only safe way to search for efficient catalysts whenever the problem arises of carrying out a desirable and thermodynamically possible chemical transformation with the help of specific catalysts.

The main reason for this situation seems to be that a full understanding of catalytic action would require, for any given case, a much deeper knowledge of the nature and action of atomic and molecular forces than we possess today. In addition, in the field of heterogeneous catalysis the fine structure of solid surfaces plays a decisive role, and much more would have to be known about the qualitative and quantitative nature of solid surfaces than we know at present. In other words, a science of catalysis has to be erected on foundations which still have to be laid.

Nevertheless, the better understanding and the mastery of catalytic action is an urgent problem and every possible effort has to be made to achieve some progress toward this aim. An essential and indispensable condition for everyone who embarks on the study of catalytic reactions,

either for purely practical or for scientific purposes, is to become thoroughly familiar with the practical know how and the scientific results which have been accumulated in this field.

This is no easy task. Most of the publications dealing with the theory as well as the practical aspects of catalytic processes are widely scattered throughout various journals and handbooks, covering the range from theoretical physics to descriptions of industrial plants. Considering this wide dispersion of papers dealing with essentially the same basic subject and considering further the practically complete separation of biocatalytic research and publications from the field of "man made" catalysts, it appeared to the editors a worthwhile undertaking to improve the possibilities and to facilitate the study of the catalytic literature by issuing, in annual sequence, collections of papers under the name *Advances in Catalysis and Related Subjects*.

Our aim for *Advances in Catalysis* is to obtain contributions from scientific and industrial workers that represent complete and detailed surveys of those specific sectors in which these authors are mainly interested and in which they have worked successfully. This not only involves treatises on the specific materials and products for which catalytic reactions have been developed, but also general reports on new scientific theories and methods which promise to become valuable for a better understanding of catalytic phenomena.

We shall try to neglect none of the various types of catalytic actions, such as the catalyses in the homogeneous gas phase and in liquids, although heterogeneous or surface catalysis will necessarily be a predominant feature of the *Advances* in view of its particular problematic aspects and its preponderant practical importance.

As to biocatalysis, no publications dealing with specialized topics are being planned for the *Advances in Catalysis* because this field is already covered by other annual publications. However, we intend from time to time to bring reports in which the relationship and parallelism between this special field and "normal" catalysis are discussed.

In view of the complicated nature and enormous variability of catalytic phenomena, it will be unavoidable that conflicting and controversial interpretations will emerge in the text of the various papers. This will illustrate the unsolved difficulties and the uncertainties which still prevail in the study of many catalytic reactions and in the discovery and production of catalysts, and may stimulate new ideas better than an enforced and unwarranted consensus of opinion.

Considering the difficult task of compiling the important features of any given sector of research in a clear but still critical fashion, the editors are greatly indebted to the response of the authors who will present the

developments in fields with which they are intimately familiar. It is our aim to obtain contributions from all parts of the world as far as the present world situation permits.

After several years *Advances in Catalysis* ought to present a compilation of papers, written by competent specialists, which should enable anybody to obtain a fairly complete concept of the practical achievements of current and new methods and of the various theoretical approaches to the manifold problems.

We hope that the *Advances* will serve a useful purpose and will have the whole-hearted support of the readers, particularly in the form of suggestions of special authors, selection of specific topics, and of other improvements.

The support and encouragement given by the publishers in this undertaking is gratefully acknowledged.

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The Heterogeneity of Catalyst Surfaces for Chemisorption

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The technological development of catalytic processes was already well advanced at the conclusion of World War I but the basis for such development was largely empirical. No large body of scientific advance in the theory of catalysis had emerged in the interval between Faraday's researches on the "power of metals and other solids to induce the combination of gaseous bodies," in 1834, and the contributions of Langmuir (1) to the kinetics of surface action which originated in his studies of the "clean-up" of gases in a tungsten filament lamp.

I. INTRODUCTION

Elsewhere (Taylor, 2) it was possible to outline the main features of the development of the basic scientific research that occurred between the two World Wars. These divided themselves naturally into four distinct periods of advance each of approximately 5 years duration. Up to 1925 research was concerned largely with the evaluation of the Langmuir concept of unimolecular adsorption of gases at the surfaces of catalysts and the consequent kinetic treatment of surface reactions. Between 1925 and 1930

attention was devoted largely to the exploration of the heterogeneity of catalyst surfaces, to the importance of "active centers" on actual catalysts and to the consequences of such centers in terms of the features of poisons and promoter action already familiar in the industrial applications of catalysis. By 1930 it was possible to differentiate between types of association between gas and catalyst surface, to distinguish, in many cases, between nonspecific, physical or van der Waals adsorption of gases which has negligible significance in the phenomenon of catalysis and, on the other hand, a chemical association between gas and surface, chemisorption, involving chemical valency forces between surface atoms and adsorbed species and requiring for the formation of the adsorption complex an activation energy of adsorption. It was in this period, also, that new tools, notably the use of para-hydrogen and the deuterium isotope, were being increasingly employed to elucidate the nature of the interaction between gas and surface and between adsorbed reactant species on such surfaces. In the final years preceding World War II, scientists in the field of surface catalysis had succeeded (Emmett and Brunauer, 3) in obtaining a measurement of the accessible surface area of catalytic materials, reproducible in different laboratories and had essayed the task of exploring the specific activity of particular crystal faces in such catalytic materials as nickel, iron, platinum, palladium and rhodium (Beeck, Smith, and Wheeler, 4) which could be produced in film forms with particular oriented faces of the crystal predominantly present in the catalyst preparation.

During the war years there is definite evidence that fundamental research in the area of contact catalysis went into eclipse. It is not yet possible to discern the direction in which new developments of the most significance will occur. We can, however, call attention to programs which tend to renew interest in the problem of heterogeneity of actual catalyst surfaces, which formed an important phase in the second five year period already mentioned and which was in sharp contrast to the attitudes prevailing immediately prior to the war. Then, there was a definite tendency to minimize all emphasis on the imperfections of crystal structure in catalysts, the distortion of faces, abnormal dimensions in the crystal lattices, extralattice structures resembling more nearly the gaseous species of an element. Rather, the properties of a catalyst were being interpreted in terms of the normal faces of particular crystals and their statistical distribution in a particular catalyst preparation.

The method of evaluating the total surface area of catalyst preparations that resulted from the researches of Brunauer, Emmett, and Teller (5) on the van der Waals adsorption of gases, such as nitrogen and butane, at temperatures near to their respective boiling points, provided a very powerful tool with which to re-examine the whole problem of "active centers" or

the heterogeneity of practical catalysts. In the period 1925-1930, when research into such matters was most intense, the scientist had no adequate measure of the extent of surface in the preparations which he studied. Intercomparison of different preparations was therefore severely limited and restricted. Nor could the extent of active surface, presumed from the studies to be present, be estimated at all in terms of total area accessible to gas. The development of the Brunauer-Emmett technique changed this condition materially for the better. It became possible for the scientist to define rigorously the extension of a surface which his particular method of preparation of a catalyst would produce and to state his conclusions concerning a particular measurement of an active area in terms of a total available area. The techniques were at hand to define a percentage efficiency of a total specified surface.

One other factor contributed to the desirability for the re-examination of the concept of active centers. The development of a distinction between van der Waals adsorption and chemisorption only occurred after the interest in heterogeneous surfaces had somewhat waned. A return to the study of heterogeneity of surfaces in the postwar years could be assisted by the sharper differentiation between the two types of adsorption that resulted from the development of the concept of and criteria for chemisorption.

As an illustration of the possibilities inherent in such studies record will be made of a group of researches now under way in the Princeton laboratories in which both measurement of surface areas and differentiation between van der Waals and chemisorption are being utilized for a restudy of the variation in the character of different catalyst preparations. Work already accomplished has permitted an evaluation of a series of oxide catalyst preparations such as have found use in catalytic hydrogenations, notably zinc oxide, chromium oxide, zinc-chromium oxide mixtures, and manganese-chromium oxide preparations. The methods of study are presently being employed in corresponding researches on the heterogeneity of metal catalysts, notably copper, iron, and nickel. The results already accumulated suggest that interesting generalizations and significant applications will follow.

II. HETEROGENEITY ON OXIDE SURFACES

1. Zinc Oxide

a. General Considerations. It was decided to re-examine the adsorption of hydrogen at various oxide surfaces. Earlier work (Taylor and coworkers, 6), in the years 1930-1938, had indicated certain advantages from such choice. In many such catalyst preparations the temperature regions in which van der Waals adsorption and chemisorption of hydrogen

occur are sharply separated one from the other due to a relatively considerable energy of activation of chemisorption on such oxide surfaces. Thus, the earlier work had revealed (Taylor and Sickman, 6b) that on zinc oxide surfaces the chemisorption of hydrogen set in measurably at temperatures above 0°C . whereas in this temperature range the van der Waals adsorption of hydrogen must be negligibly small. A result, obtained in that earlier work (Taylor and Strother, 6c) provided an additional incentive for a restudy of zinc oxide preparations. Zinc oxide, prepared from the oxalate, had shown in the region of chemisorption two maxima of chemisorbed gas at temperatures in the neighborhood of 80 and 218°C . With the exception of two similar maxima observed by Emmett and Harkness (7) in the chemisorption of hydrogen on iron synthetic ammonia catalysts, and labelled by them type A and type B chemisorptions, these maxima in the zinc oxide adsorptions of hydrogen were without parallel. The interpretation of two types of chemisorption of hydrogen on a catalyst surface has not, thus far, been satisfactorily formulated. It was, therefore, decided to restudy the whole problem of hydrogen adsorption on zinc oxide, ex-oxalate, securing simultaneously the pertinent Brunauer-Emmett-Teller (B.E.T.) data as to total accessible surface on the preparations examined.

b. Technique. The method of study chosen was to measure at successively increasing temperatures from -195°C . (liquid nitrogen temperature) to 302°C . the extent of adsorption of hydrogen, the working pressure being maintained continuously at about 1 atmosphere pressure (Taylor and Liang, 8). In the temperature range below 0°C . the measurements revealed a steadily decreasing adsorption with increasing temperature as would be anticipated for van der Waals adsorption. Above 0°C . a phenomenon of considerable importance became evident. In this temperature range where van der Waals adsorption is negligible it was found that, in passing from one operating temperature to another, higher temperature, marked desorption of gas occurred, to be followed after a measurable interval of time by a readsorption of the gas. The desorption process was relatively rapid, the readsorption was a typical rate process of chemisorption. An example of such an observation is plotted in Fig. 1.

The diagram further indicates that after the rate of adsorption, subsequent to the change of temperature from 111 to 154°C . had become negligibly slow, a return to the lower temperature, 111°C ., resulted in the rapid readsorption of gas in an amount corresponding closely to that which had been desorbed when the temperature was elevated through the given interval. This observation suggests immediately that, during the temperature rise, gas has been desorbed from a given area of the surface on which it was held (by chemisorption, it can be shown) at the lower temperature.

The surface laid bare by the desorption apparently remains bare at the higher temperature, although adsorption proceeds at this higher temperature, presumably therefore on other areas of the total surface. When the

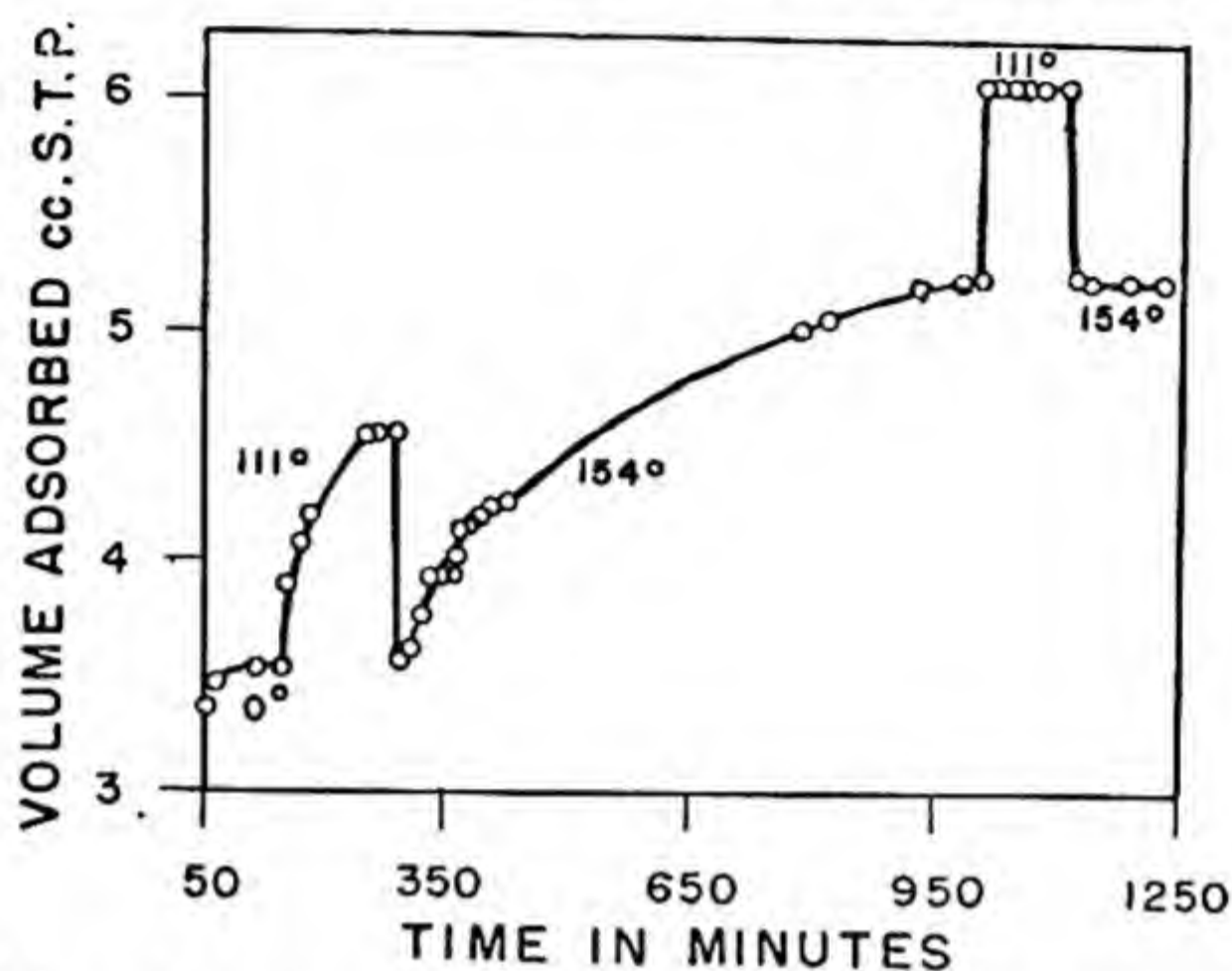


FIG. 1. Adsorption rate curve on raising and lowering temperature (hydrogen on ZnO I).

temperature is lowered, the bare surface immediately refills with chemisorbed gas at a rapid rate in agreement with the observation that it was rapidly desorbed when the temperature was elevated.

This phenomenon of rapid desorption on raising the temperature followed by a slow readsorption on other areas was consistently observed

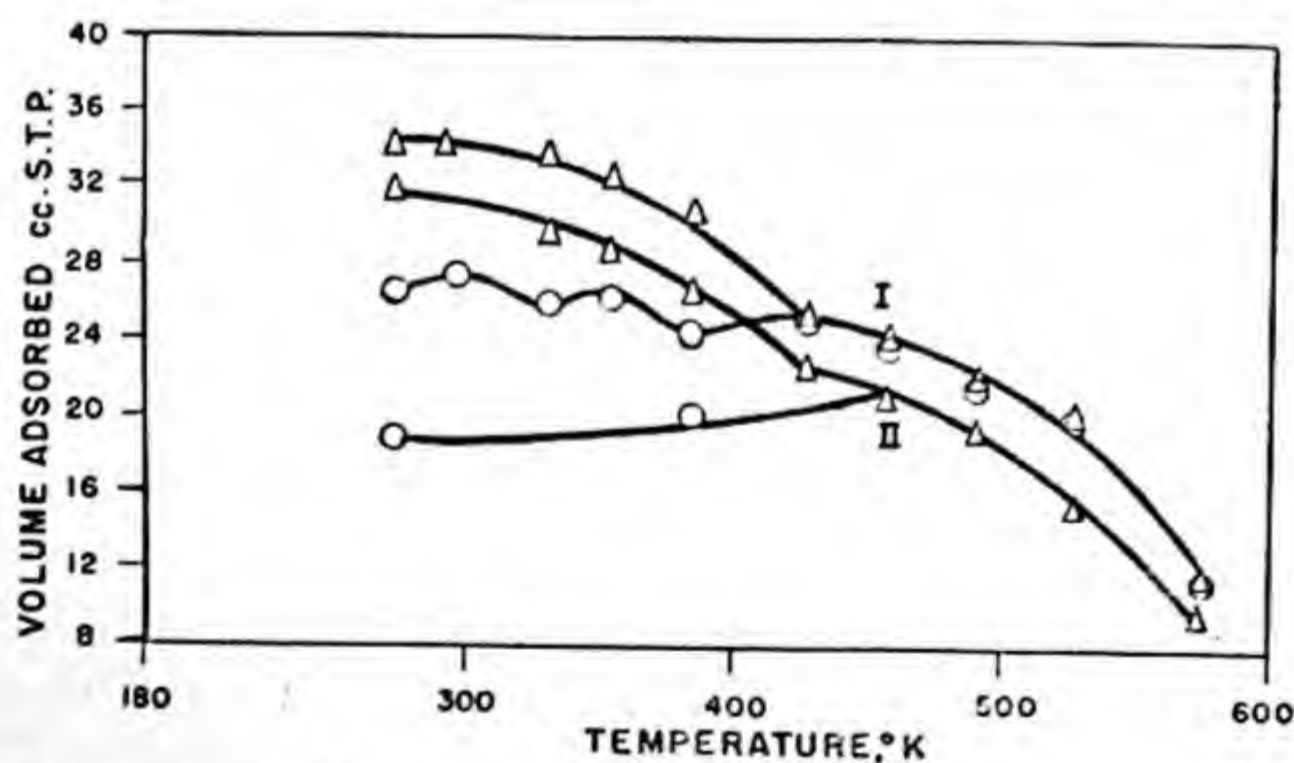


FIG. 2. Adsorption isobar (hydrogen on ZnO III). Roman numeral indicates order of run.

O: Raising temperature

Δ: Lowering temperature

in the case of zinc oxide chemisorption at temperatures between 56 and 218° C. This led to an examination of the behavior of the preparation as it was cooled in hydrogen at 1 atmosphere pressure from 302° C. to liquid nitrogen temperatures. An isobar for zinc oxide on raising and lowering the temperature through these ranges is shown in Fig. 2. The increments of adsorption on lowering the temperature through a given interval roughly paralleled the rapid desorptions that occurred as the temperature was raised through the same interval.

That the adsorptions involved were actually due to chemisorption was indicated by measurements of nitrogen adsorption on the zinc oxide surfaces studied. These measurements showed that already at 56° C. the van der Waals adsorption of nitrogen was too small to measure on zinc oxide surfaces with surface areas by the BET method in the neighborhood of 5–25 sq. meters/g. The van der Waals adsorption of hydrogen would be still smaller and lower by one or more orders of magnitude than the quantities of gas involved in the desorption and readsorption processes.*

2. Other Oxides

These observations, when extended to other oxides or mixtures of oxides, gave in part confirmatory data and, in one case, that of manganese-chromium oxide, data which significantly differed from those obtained with zinc oxide. Thus, with chromium oxide gel with a surface area of 189.5 sq. meters/g. the quantities of gas involved in the desorption-readsorption phenomena between 56 and 302° C. amounted to 9 cc. or nearly 5% of the total surface. With a zinc chromium oxide of 21 sq. meters/g. the area involved in desorption-readsorption phenomena was 13% of the total surface between 0 and 302° C. With manganese-chromium oxide, on the other hand, no readsorption of gas was observed when the sample was cooled in hydrogen from 218 to 0° C.

3. Interpretation of the Data

A schematic representation of these several conditions can be seen from Fig. 3. If the continuous lines *AB* and *CD* represent true equilibrium isobars for van der Waals and chemisorption respectively, it is obvious that, on raising and lowering the temperature in the *CD* region the same experimental values will be obtained. If the dotted line *BC* represents values obtained while the temperature is being raised it is obvious that these are below the true equilibrium values because the latter cannot be reached in practicable times of observation since the velocity is too low. If the

* This arises from the identity of the van der Waals forces between gas molecules and the van der Waals forces between gas molecules and surfaces resulting in stronger adsorptions of the more easily liquefiable gas.

surface were so uniform or the hydrogen held so strongly that no desorption had occurred in the ascending portion BC the adsorption data which would be obtained on cooling below the point C would be *horizontal* until the van der Waals adsorption set in again. This is indicated by the horizontal section CE and the ascending section EF . This is the case to which man-

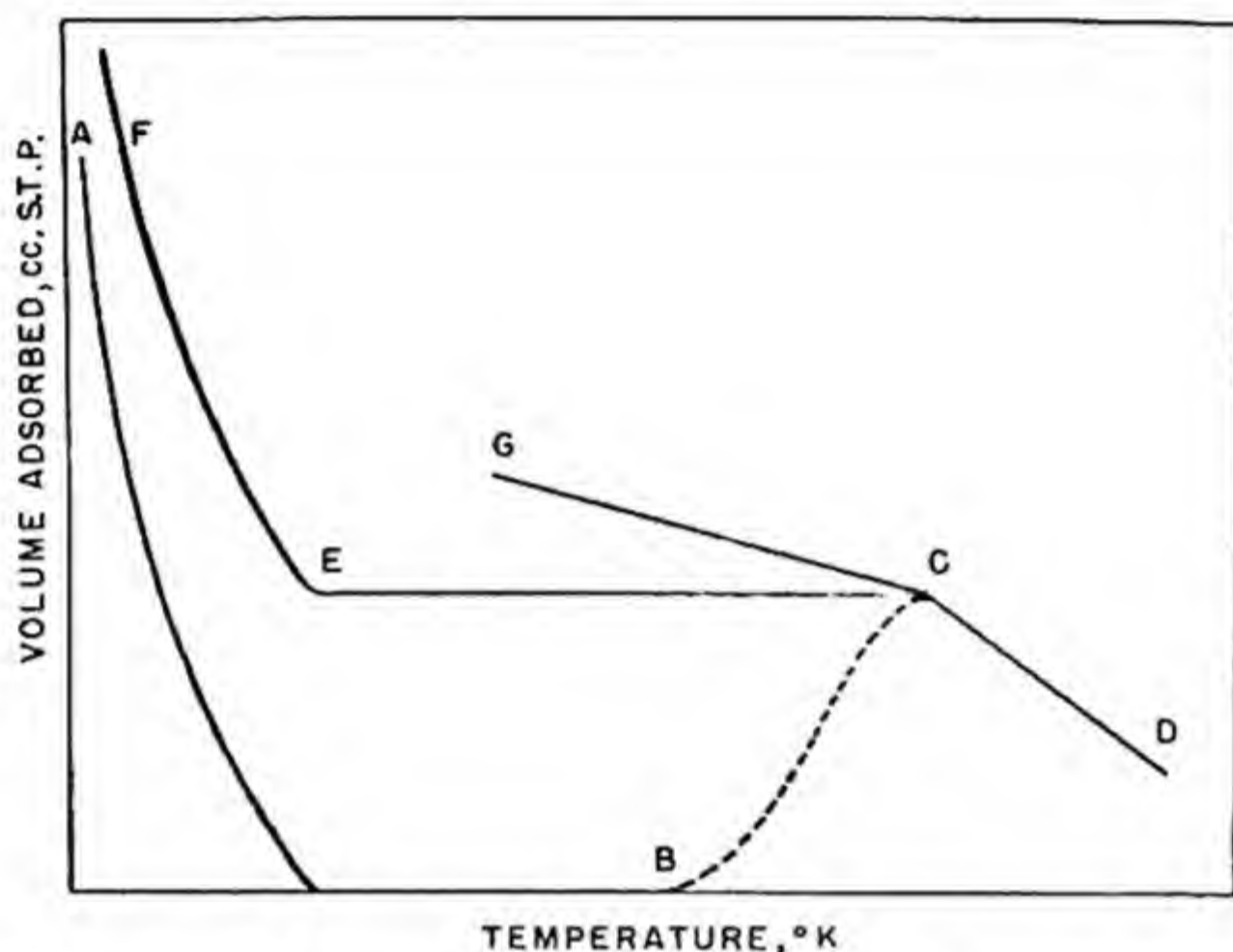


FIG. 3. Schematic representation of chemisorption on lowering temperature with uniform and heterogeneous surface.

ganous-chromium oxide conforms, for the probable reason that the chemisorption of hydrogen by this surface is strong with a heat of adsorption of ca. 20 kcal./mole and an activation energy of 10 kcal./mole (Taylor and Williamson, 6a). The rate of desorption with an activation energy of ~ 30 kcal./mole would be small in the ascending section BC of the curve.

When, however, desorption does occur in the ascending portion of the curve BC , there should, on cooling down from C , no longer be a horizontal section CE but continuously increasing values of the adsorption CG , measuring, in excess of the values over the horizontal section, the quantity of gas which was desorbed during the measurements made in passing upwards in temperature from B to C . It is this behavior which is shown by zinc oxide, chromium oxide gel, and zinc-chromium oxide.

This aspect of heterogeneity of surface which the desorption-readsorption phenomena reveal is worthy of a more detailed analysis. Consider, for example, a hypothetical adsorbent, having two distinct adsorbent areas A and B , characterized by two distinct activation energies E_A and E_B , and two characteristic heats of adsorption λ_A and λ_B . It is possible to conceive two temperatures T_1 and T_2 such that, at the lower temperature

T_1 only the area A will be filled while B remains sensibly bare, whereas at the higher temperature T_2 the area A will be bare and area B will be sensibly covered. These two possibilities are illustrated in Fig. 4. The requisite

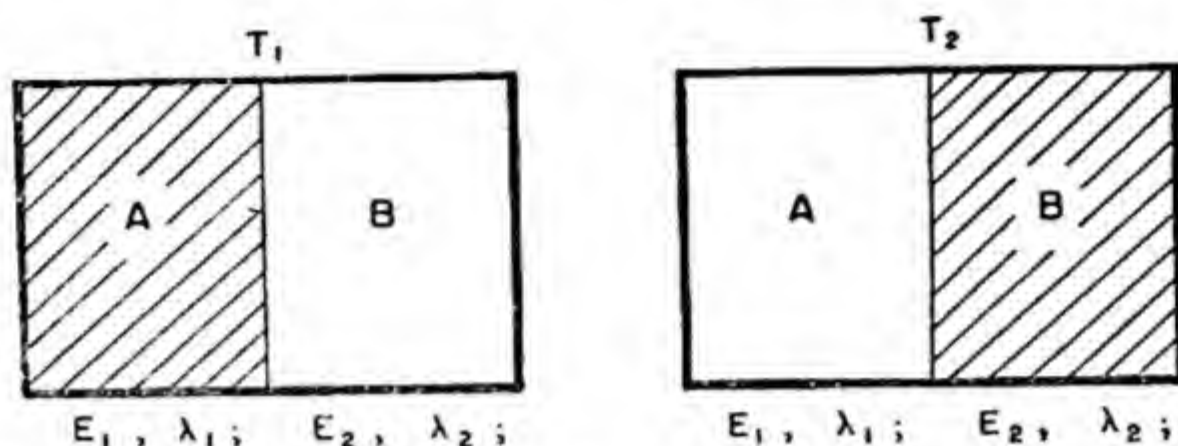


FIG. 4. Hypothetical adsorbent with two areas of different characteristics.

conditions are the following. If, at T_1 , the magnitude of the activation energy E_A is sufficiently low and λ_A sufficiently high the area A will be progressively covered with time. The condition for B to remain sensibly bare is that E_B be sufficiently large so that negligible chemisorption occurs due to the smallness of the Boltzmann factor e^{-E_B/RT_1} in the equation for the velocity of chemisorption. For the reversal of this condition at temperature T_2 the necessary conditions are, (1) that the magnitude of $(E_A + \lambda_A)$, the energy of desorption from area A , shall be low enough to permit rapid evaporation from this area, and (2) that E_B shall be of such a magnitude that chemisorption shall occur with measurable velocity, and $(E_B + \lambda_B)$ be sufficiently large that the surface shall be progressively covered.

Given such conditions it would obviously be possible to select a working pressure P such that at T_1 the fraction θ of a given surface covered will approach $\theta_A = 1$ while $\theta_B \sim 0$; at T_2 , $\theta_A \sim 0$ and θ_B approaches unity. Furthermore, at such a pressure P , the composite adsorbent $A.B$ saturated on the area A at T_1 would, on changing the temperature to T_2 , suffer desorption of gas from area A and adsorption eventually would reach saturation on B . If the desorption process were more rapid than the readsorption process the observer would record, on raising the temperature, first an evolution of gas and then a readsorption. It is this phenomenon which is characteristic of the result already outlined with oxides and with some metals as next to be recorded. It should be emphasized that with all actual adsorbents the conditions will never be as simple as those discussed in the hypothetical adsorbent. The more complex surfaces will show a more complex pattern of behavior, actually an integration of both desorptions and adsorptions, each with its own characteristic velocity on a particular surface.

Activation Energy of Chemisorption on Heterogeneous Surfaces. A further consequence of a heterogeneity of surface such as is indicated in

Fig. 4 has also been pointed out by Taylor and Liang (8a). Measurement of the velocity of adsorption of a given gas on a clean surface AB at temperature T_1 would record the amount of gas adsorbed with time on area A only. At temperature T_2 the measurement would record the rate of adsorption on area B . The two velocities would actually have no relation to each other. They should not be used to determine activation energies by means of the equation

$$\ln \frac{v_2}{v_1} = \frac{E_{act}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where v_1 and v_2 are the measured velocities at the two temperatures. Because the processes at each temperature occur on different areas they actually have no connection with each other. They cannot be used for determining the activation energy of a process because they are two distinctly different processes. Conversely, if from velocity data at three or more temperatures strongly varying values for the activation energy of adsorption of a given volume of gas are obtained, the data are direct evidence of the heterogeneity here under analysis. The early data of Taylor and Strother (6c) reveal this, while the later data of Liang (8b) are much more emphatic evidence of the same condition in the case of zinc oxide.

III. HETEROGENEITY ON METAL SURFACES

1. Copper

In Figs. 5 and 6 are reproduced data for copper catalysts which show desorption-readsorption phenomena and also the variation in a hydrogen adsorption isobar on raising and lowering the temperature. Catalyst B-1 of Fig. 5 was a copper-magnesium oxide catalyst obtained by coprecipitation of the oxides and reduction of the copper to metal in hydrogen at 350° C. The adsorption of hydrogen was qualitatively similar to that obtained by Lewis and Taylor (9). The data reveal the desorption-readsorption phenomena at 56 and 302°. Catalyst B-4 was prepared from a nitric acid solution of 63 g. copper containing less than 0.0005% nickel but with the addition of 0.01 mole thorium nitrate. The solution was evaporated to dryness and ignited to oxide, after which reduction was effected at 154° C. The thorium nitrate served to maintain some extension of the surface. A pure sample of copper nitrate ignited and reduced at 280° C. gave a surface area of 0.04 sq. meters/g. A pure sample reduced at 110° C. over a period of 10 days gave an area of 0.74 sq. meters/g. With the addition of 0.01 mole thorium nitrate/mole of copper the surface, after reduction at 154° C., was 2.86 sq. meters/g.

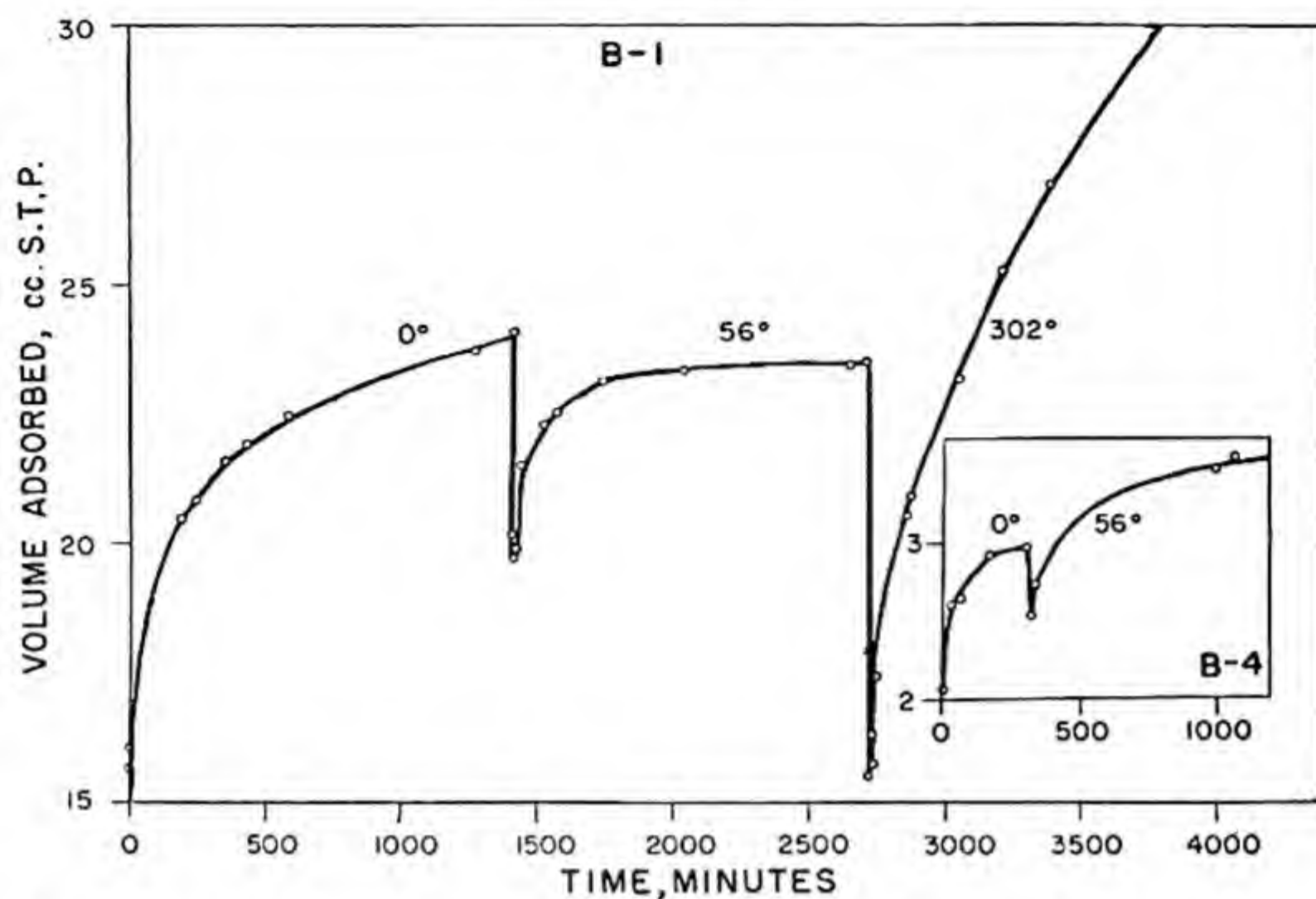


FIG. 5. Hydrogen adsorption rates on copper catalysts at 1 atmosphere.

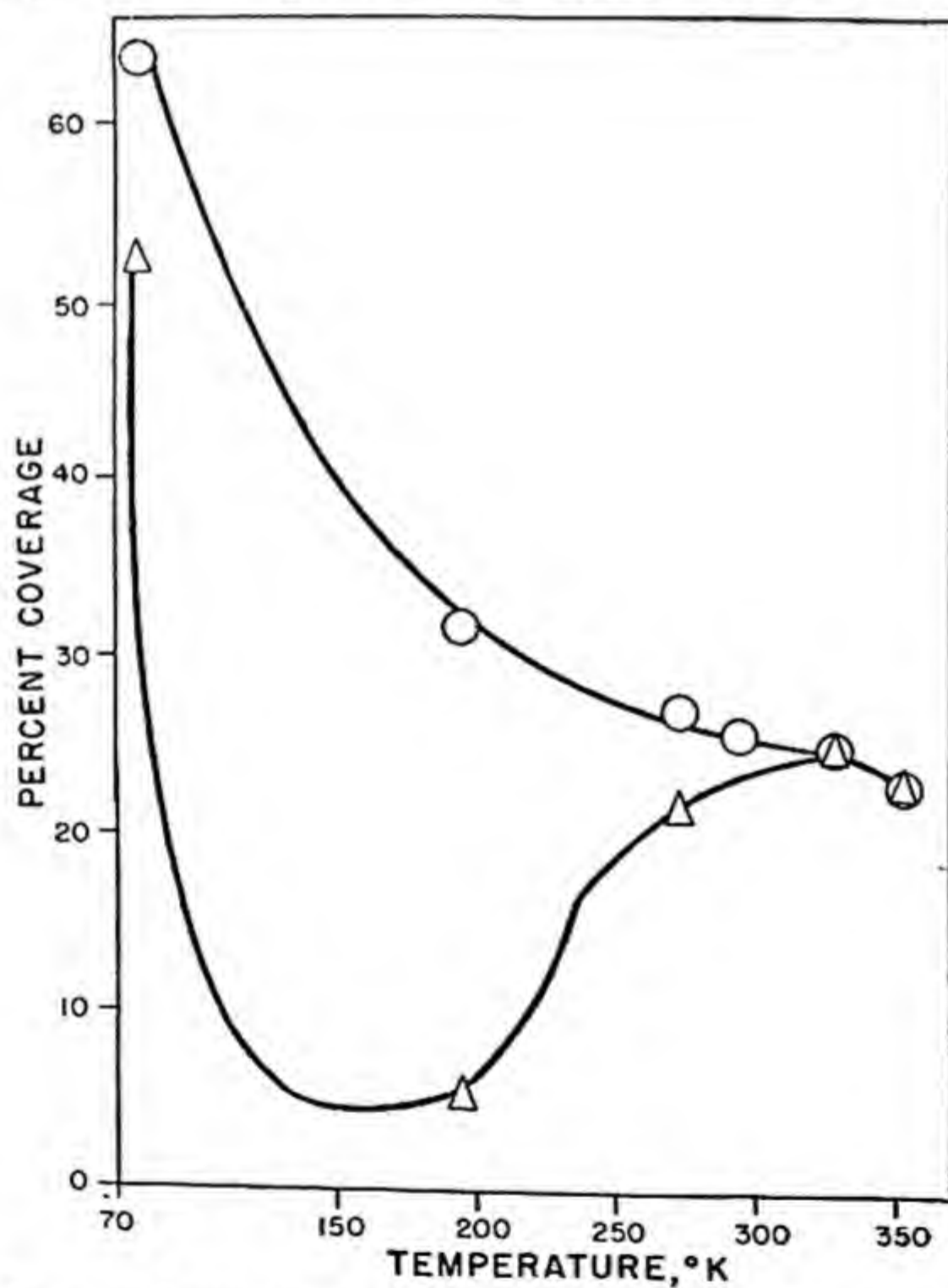


FIG. 6. Hydrogen adsorption isobar on copper B-4 at 1 atmosphere. $V_m = 13.6$ cc.
O: Lowering temperature
Δ: Raising temperature

The data illustrated in the two diagrams are evidence that the same phenomenon of desorption and readsorption is found with copper catalysts, either supported or essentially pure metal, as is found with the oxides.

2. Iron

With doubly-promoted iron synthetic ammonia catalysts the same type of observations are repeated. Data on desorption and readsorption are shown in Fig. 7, while in Fig. 8 are the values obtained on raising and lowering the temperature. It will be noted that the latter curves do not show the double maxima at -78 and 110°C . earlier found by Brunauer and Emmett (10) and examined by them in detail as types *A* and *B* adsorption.

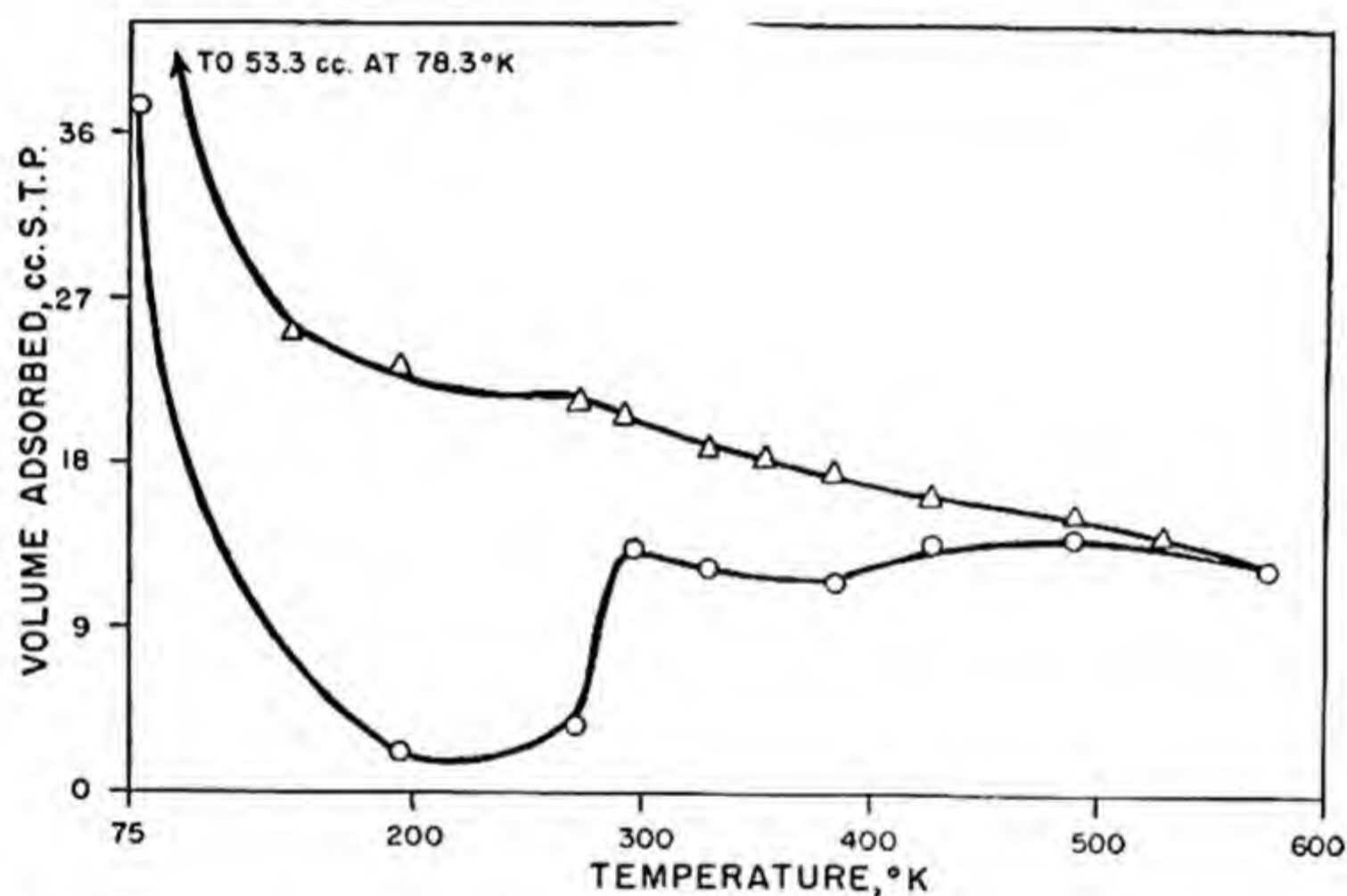


FIG. 7. Isobaric hydrogen adsorption on iron CF 413-9 at 1 atmosphere.
O: Raising temperature Δ: Lowering temperature

The present curve does not show the maximum found by the previous authors at -78°C . Private communication from Dr. Paul Emmett indicates that the possible explanation for this is that the reduction procedure here employed may have failed to reduce the iron in those areas where the low temperature chemisorption of hydrogen occurs. According to Emmett these areas are only uncovered by reduction at around 500°C . in a rapid stream of hydrogen freed from oxygen and well dried before passing into the reduction zone. The data in Fig. 7 do, however, show that from room temperature upwards there is always evidence of desorption on raising the temperature followed by readsorption, and the

data shown in Fig. 8 for lowering temperature serve to confirm these observations. The iron catalyst used was a technical synthetic ammonia catalyst containing only 1-2% of the potash-alumina promoter.

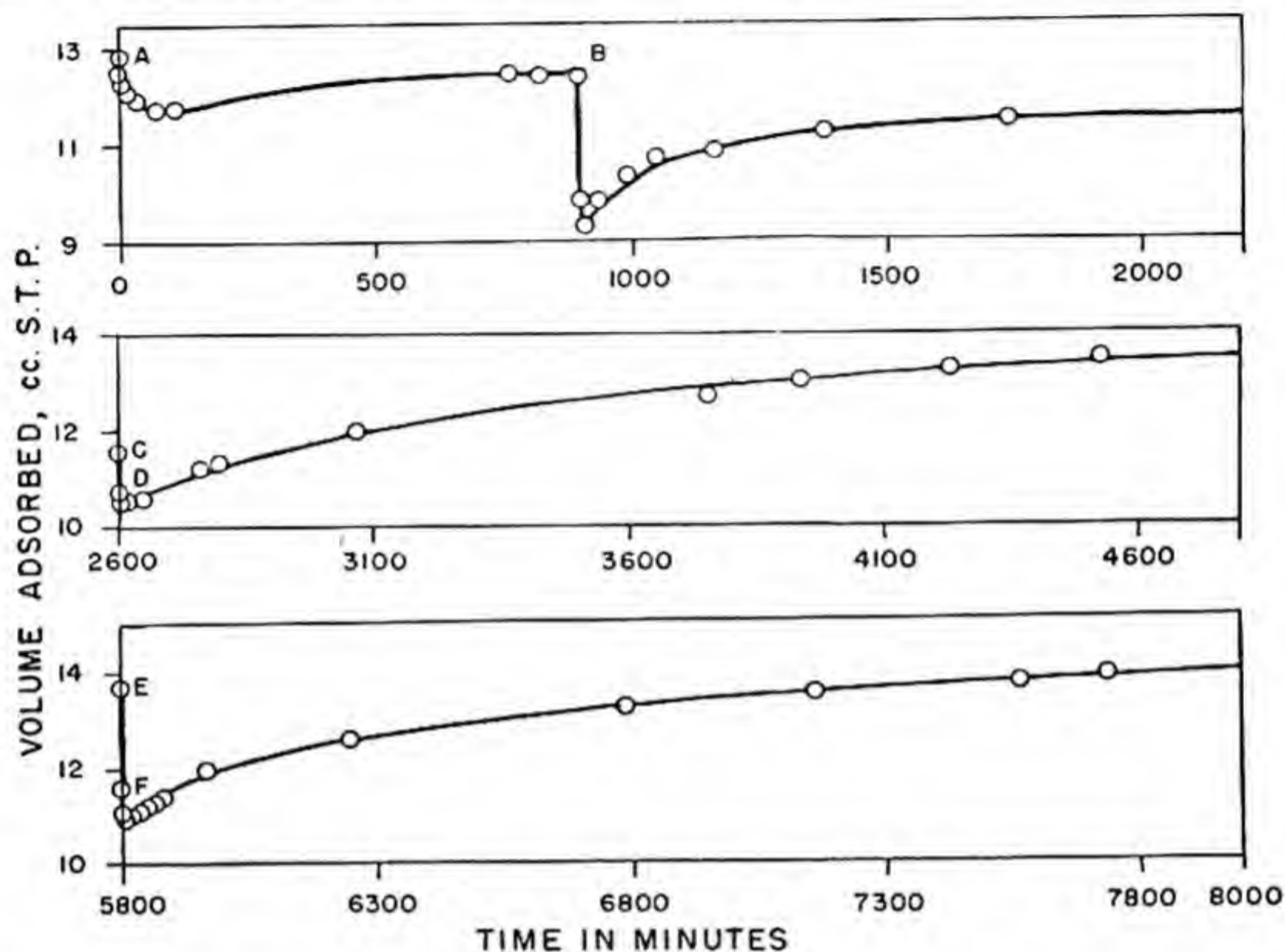


FIG. 8. Rate of hydrogen adsorption on iron CF 413-9 ($V_m = 67$ cc.) at 1 atmosphere (13.4 cc. adsorbed at 24° in 8 days before A). First reading at: A, 56° ; D, 154° ; F, 218° . Change temperature at: B, 56 to 111° ; C, 111 to 154° ; E, 154 to 218° .

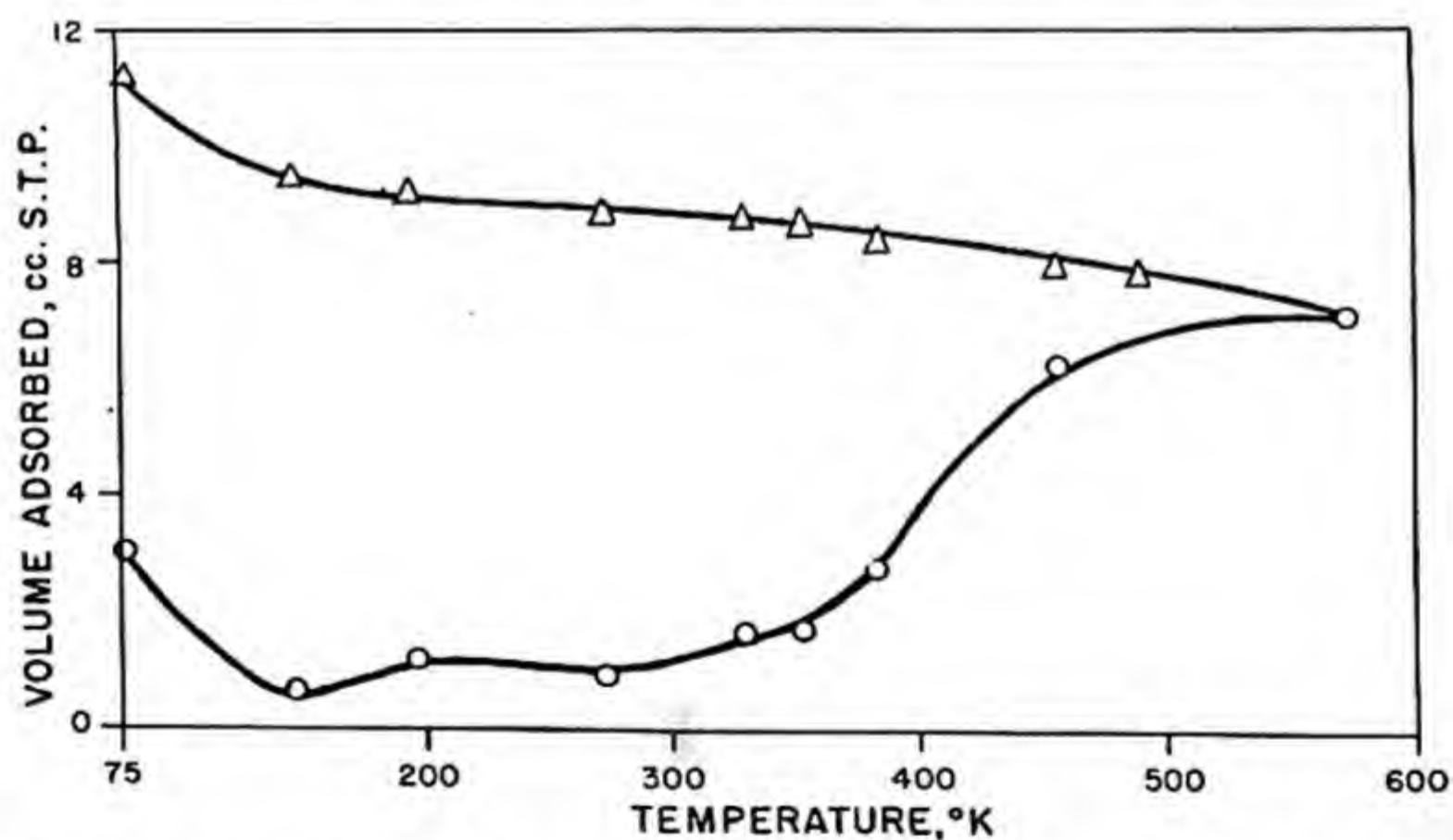


FIG. 9. Isobaric hydrogen adsorption on iron 931 at 1 atmosphere. $V_m = 7.58$ cc.
O: Raising temperature Δ: Lowering temperature

In Fig. 9 are shown comparable data with a small sample of the Fixed Nitrogen Laboratory Catalyst No. 931. Here there is some evidence of a maximum around -78°C . The curve for lowering temperature is evidence for the phenomenon of desorption-readsorption.

3. Nickel

The most extensive experiments on the behavior of nickel catalysts have been carried out by Mr. H. Sadek. The results will appear in his forthcoming dissertation and later in the scientific journals. The results may here be summarized.

Since the researches of Benton and White (11) it has been well known that chemisorption occurs on technical nickel catalysts at temperatures only slightly above liquid air temperatures. On nickel films of the type produced by Beeck (4a) it is well known that even at liquid air temperatures the hydrogen adsorption observed is chemisorption. For these reasons Sadek has made a particular study of the adsorption of hydrogen on a variety of nickel catalysts prepared by usual technical catalyst techniques and has examined them in particular detail in the temperature range from -195 (liquid nitrogen) to -78°C . (CO_2 point). He has found that adsorption studies can be carried out at the melting points of methylcyclohexane and toluene, i.e., at -126 and -95°C ., where the rates of chemisorption are especially interesting with some of the nickel preparations studied.

a. Nickel Kieselguhr. In Fig. 10 are shown measurements made on a nickel-kieselguhr catalyst (15% Ni) from a large batch prepared for us many years ago by the E. I. du Pont de Nemours Company and which has been used in many earlier Princeton studies of the catalytic activity of nickel, notably by Morikawa (12) and more recently by Kemball (13). The sample employed in the present studies was reduced at temperatures up to 400°C . and examined in the temperature range -195 to 302°C . The sample used for the work shown in Fig. 10 had a surface area measured with nitrogen equal to a monolayer of 50 cc., i.e., 85.5 sq. meters/g. on the 2.55-g. sample.

Figure 10 shows the isobars obtained starting with a clean surface at the several temperatures of -126 , -95 , and -78°C . and separate isobars representing the data obtained 10, 60, 120, and 250 minutes after hydrogen at 1 atmosphere pressure was introduced to the evacuated sample. It will be noted from the 10-minute isobar that already at -126°C . the van der Waals adsorption of hydrogen is low. Actually it must be less than the value after 10 minutes if any chemisorption has occurred. The van der Waals adsorption of hydrogen must be still lower than the -126°C . value at the higher temperatures of -95 and -78°C . Nevertheless the 10-

minute readings at these temperatures are much higher than at -126°C. , which indicates that at these temperatures chemisorption has occurred more rapidly than at -126°C. Chemisorption is occurring in these temperature intervals at measurable rates and this is illustrated by the rate

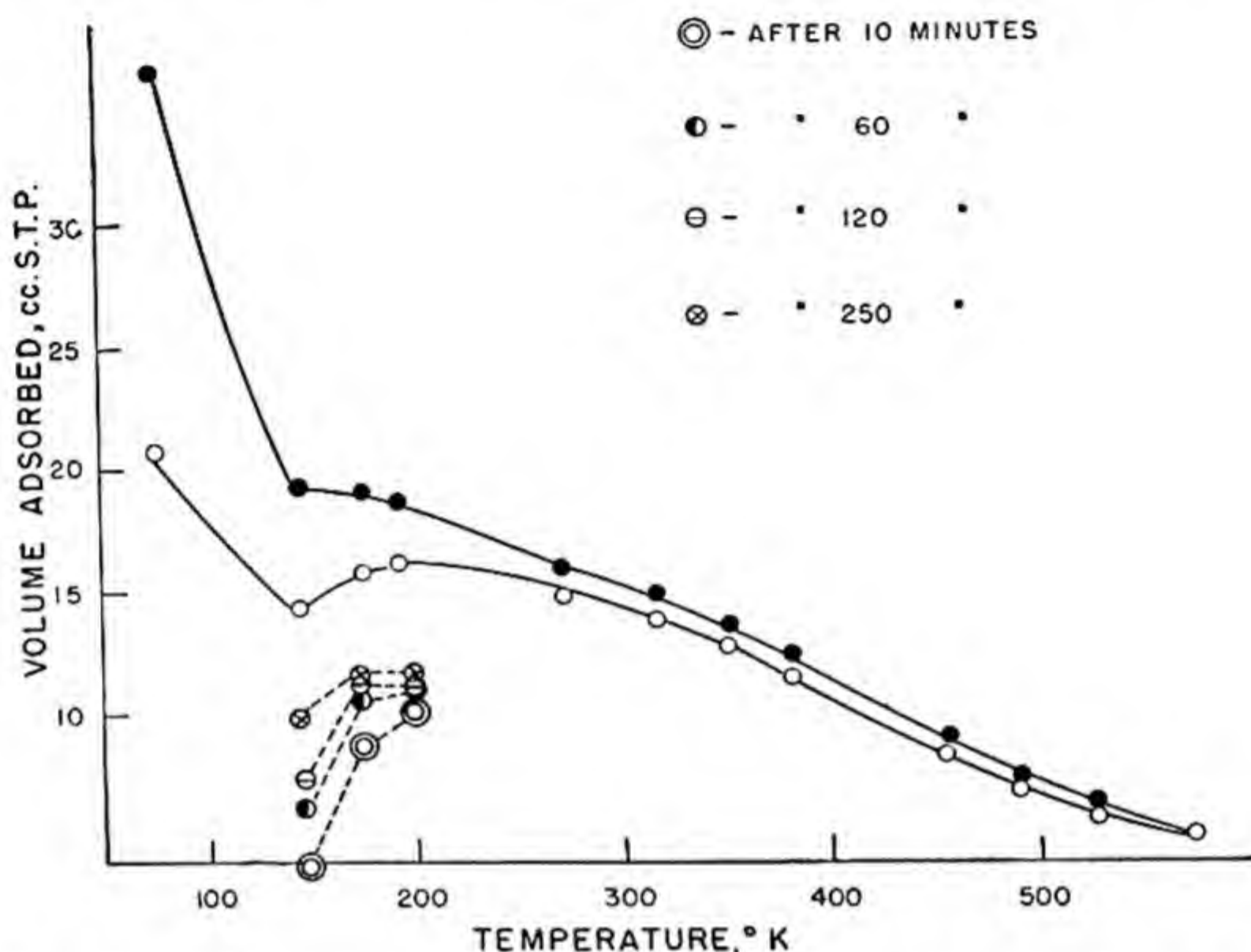


FIG. 10. H_2 Adsorption isobar of nickel kieselguhr (Du Pont). $V_m = 50$ cc.

data in Fig. 11. These rate data are in every way similar to those obtained with zinc oxide and other oxides in the temperature regions of 56 to 302°C. They are measurable at -126 to -78°C. because the activation energy is lower; but, nevertheless, an activation energy is required and determines the rate process.

Especial attention should be directed to the lower of the two isobars represented by the full lines drawn through the experimental points from -195 to 302°C. This was obtained by making first a measurement at liquid nitrogen (-195°C.) and, when saturation was apparently reached, changing the temperature successively to -126 , -95 , -78 , 0 , and so on until the temperature of 302°C. was reached. This curve is analogous to those in the preceding cases of the oxides and metals designated as points on "raising" the temperature. The upper curve represents the data obtained on lowering the temperature. It will readily be seen that between 0 and 302°C. the true equilibrium isobar is approximately reached. Below 0°C. , however, the equilibrium isobar is not attained by the technique of

"raising" the temperature while maintaining constant atmospheric pressure.

It is interesting to observe parenthetically that, for example, at -126°C . the volume of hydrogen adsorbed on a clean surface even after

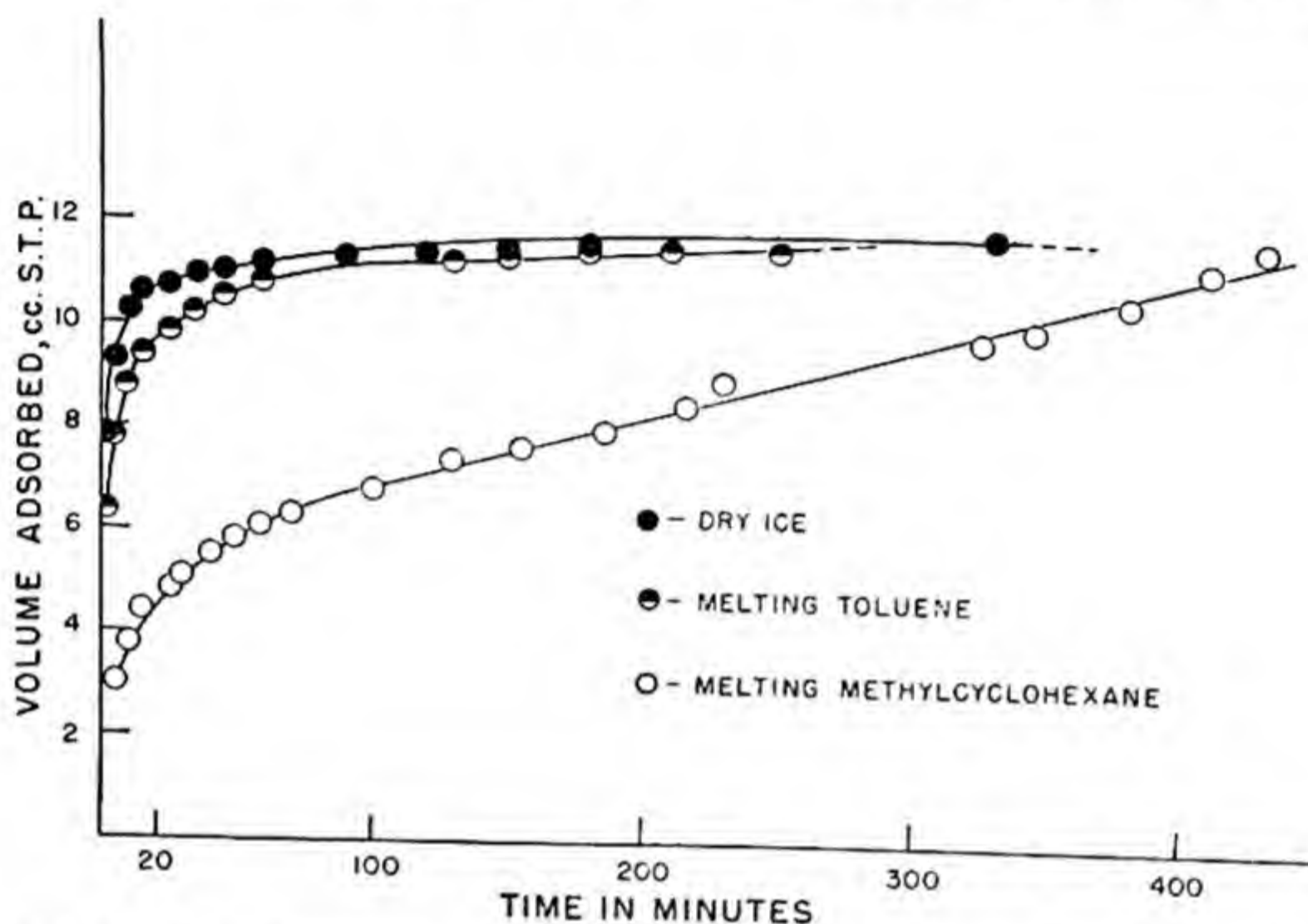


FIG. 11. Rate of adsorption of H_2 on clean surface of nickel kieselguhr (Du Pont).
 $V_m = 50$ cc.

250 minutes (and even after 400 minutes as the rate curve of Fig. 11 shows) is markedly lower than the value obtained after only 150 minutes when the system is brought up to -126°C . from liquid nitrogen temperatures. This is not an isolated example. There are numerous similar data in other surfaces studied. The nickel-kieselguhr surface is covered with hydrogen to an extent equalling nearly one-half a monolayer of nitrogen at liquid nitrogen temperatures. The high value recorded at -126°C . on raising the temperature compared with that obtained after 250 minutes on a clean surface at -126°C . suggests that, during the interval of time as the temperature is rising from -195 to -126°C ., much of the van der Waals adsorbed hydrogen is converted to chemisorbed gas and held by the surface in this manner. As already observed, the extent of van der Waals adsorbed hydrogen at -126°C . cannot exceed that recorded after 10 minutes on a clean surface. These observations are indicative of the truth of an assumption frequently made in the Princeton work that the process of chemisorption involves an activation energy effect on a surface-van der Waals adsorption complex. Actually, in 1932 it was pointed out (Taylor, 14) that on any

reasonable assumption concerning the extent of zinc oxide surfaces, with activation energies of the magnitudes observed (10–15 kcal.) the velocities of chemisorption were entirely too low to be explained on the assumption that the rate of adsorption was determined by the number of gas molecules striking the surface per unit of time and having the required activation energy in the form of kinetic energy. The present data support an assumption of an activation of a surface-van der Waals adsorption complex.

b. Sintered Nickel-Kieselguhr. Returning to the problem of heterogeneity in such nickel surfaces it is calculable from the rate data in Fig. 11 as well as from a comparison of the curves obtained by raising and lowering the temperature in Fig. 10 that, within the temperature range -126 to 0°C. , the principal heterogeneity of the nickel surface is observed. This is confirmed by the measurements recorded in Fig. 12 for the same nickel-

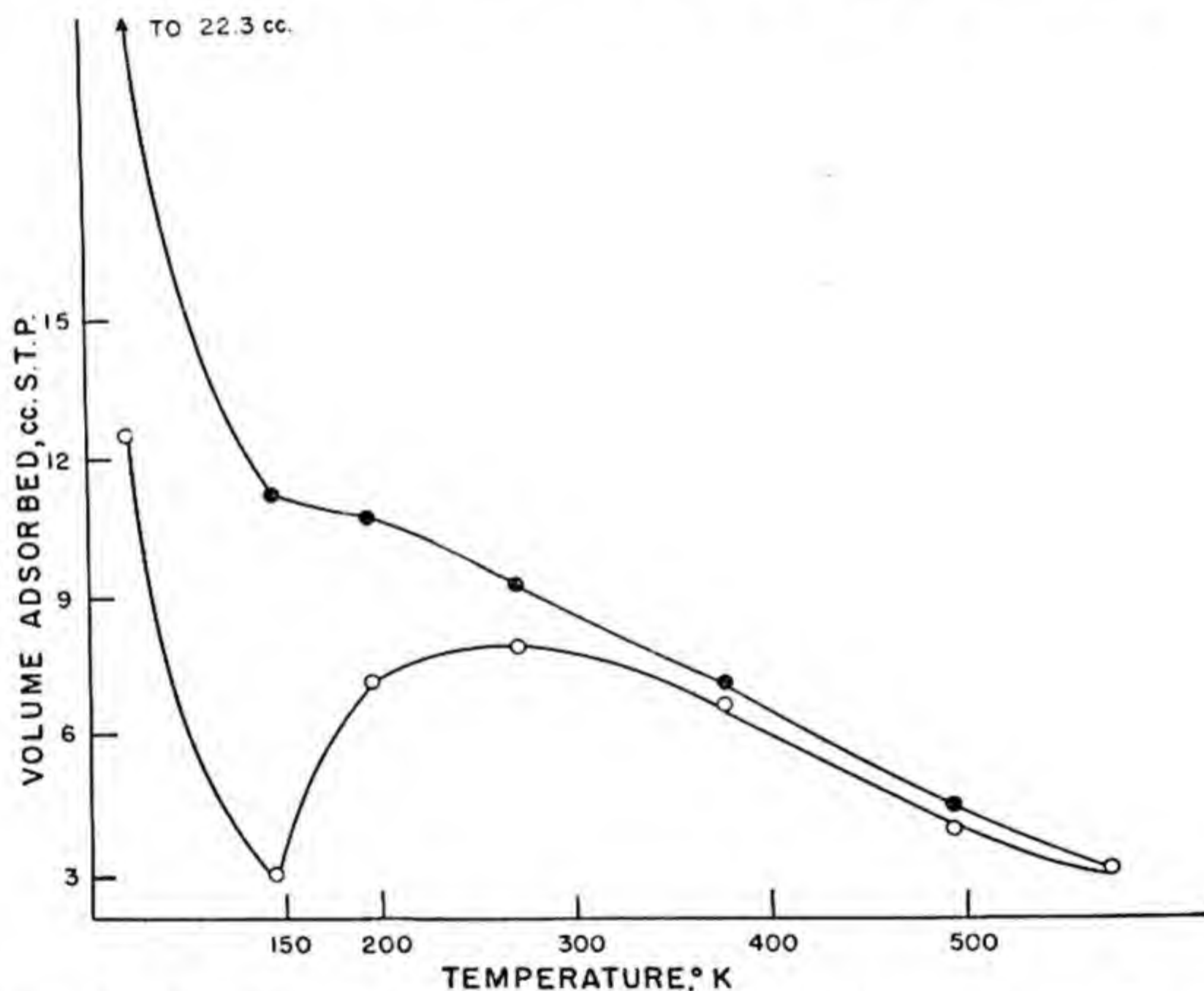


FIG. 12. Adsorption isobar of H_2 on "sintered" nickel kieselguhr (Du Pont).
 $V_m = 33.77$ cc.

kieselguhr catalyst after it had been "sintered" by heat treatment for 24 hours at 500°C. This sintering resulted in a loss of surface area indicated by the new nitrogen monolayer value of 33.77 cc., a decrease of 33% in the available surface. In Fig. 12, the van der Waals adsorption of hydrogen has decreased below that in Fig. 10 by a similar amount. At -126°C. ,

on the "rising temperature curve," the minimum of adsorption observed at -126°C . amounts to some 20% of that obtained at the same temperature on the unsintered catalyst by the rising temperature technique. This means that the chemisorption requiring only low activation energies has been suppressed by the sintering operation. There is a notable decrease in the low activation energy areas. The divergence between the "rising temperature curve" and the lowering temperature curve sets in, not at about 0°C . as with the unsintered sample but somewhere between 0 and 110°C . Figs. 10 and 12 effectively illustrate a redistribution of the heterogeneity of the surface brought about by the process of sintering by heat treatment.

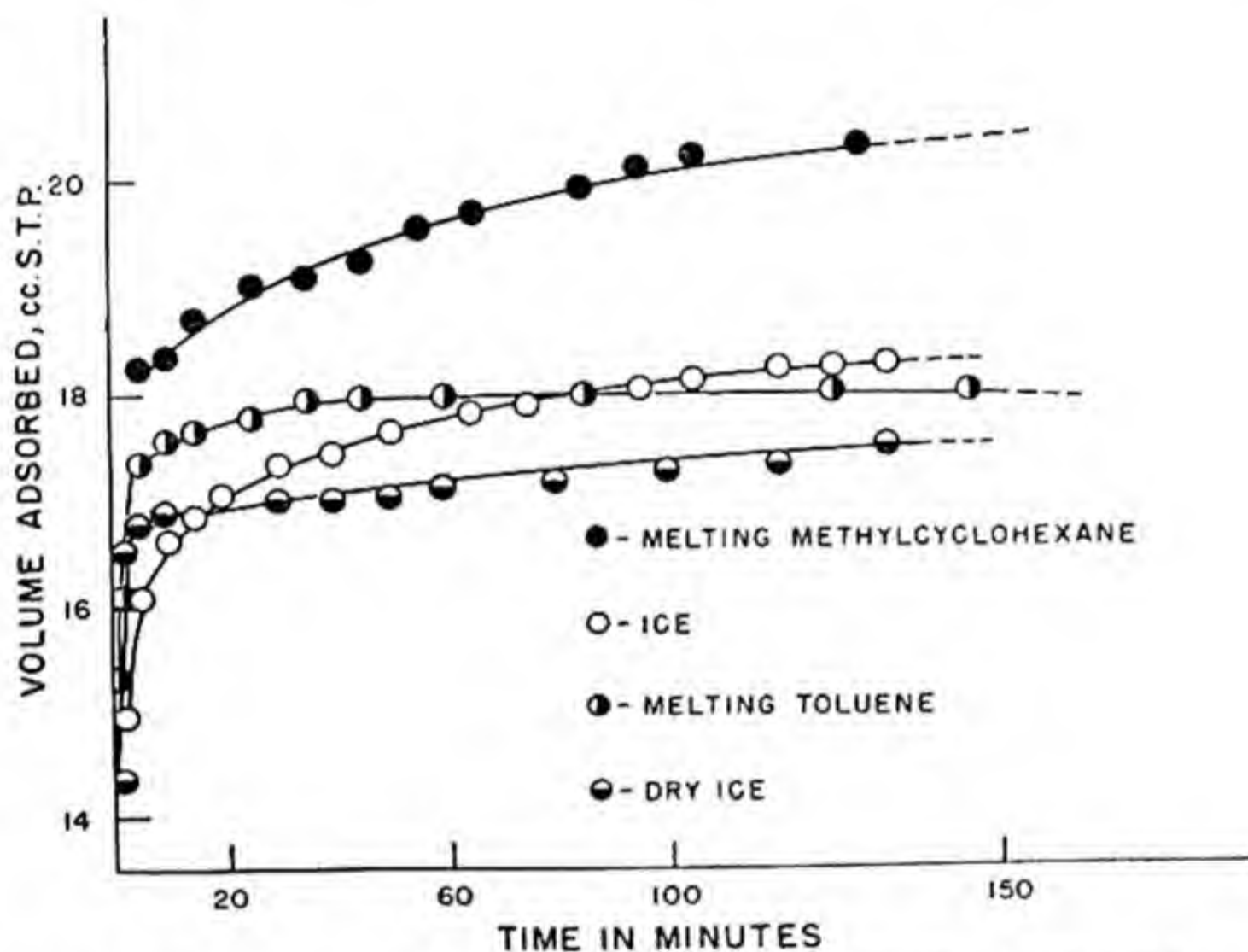


FIG. 13. Rate of adsorption of H_2 on clean surface of $(\text{Ni}-\text{ThO}_2\ 2\%)$.
 $V_m = 29.82\text{ cc.}$

c. Nickel-2% Thoria. Changes in the distribution of heterogeneity on nickel surfaces can also be secured by differing techniques of preparation. Two examples in illustration of this may be cited from among a number of such cases which will be detailed in the chemical journals. A preparation of nickel containing 2% thoria as promoter, obtained by evaporation of the nitrate solution calcination to oxide and reduction in hydrogen, was more active for chemisorption of hydrogen in the low temperature range than was the nickel-kieselguhr unsintered preparation already discussed. The rate data shown in Fig. 13 show a more rapid rate of chemisorption of hydrogen at -126°C . than in the case of nickel-kieselguhr. At -95°C ., the rate of

chemisorption is so rapid that saturation is reached within 40 minutes of the start of the determinations, in contrast to the data at this temperature shown in Figs. 10 and 11. The contrast in disposition of the rate curves at the temperatures -126 , -95 , and -78°C . in Figs. 11 and 13 is definite evidence of the different distributions of heterogeneity in the two nickel surfaces. With the nickel-thoria catalyst there is definite evidence also that at 0°C . new areas are opened up to chemisorption of hydrogen not available at the lower temperatures.

d. Nickel-Chromia. In marked contrast to the three preceding examples of nickel catalyst is the example of a nickel-chromia catalyst containing 80% nickel and 20% chromium oxide. This catalyst, which has been found to have desirable hydrogenation characteristics and some measure of technical application, is entirely different in adsorption characteristics from the preceding examples. The curves in Fig. 14 suggest at

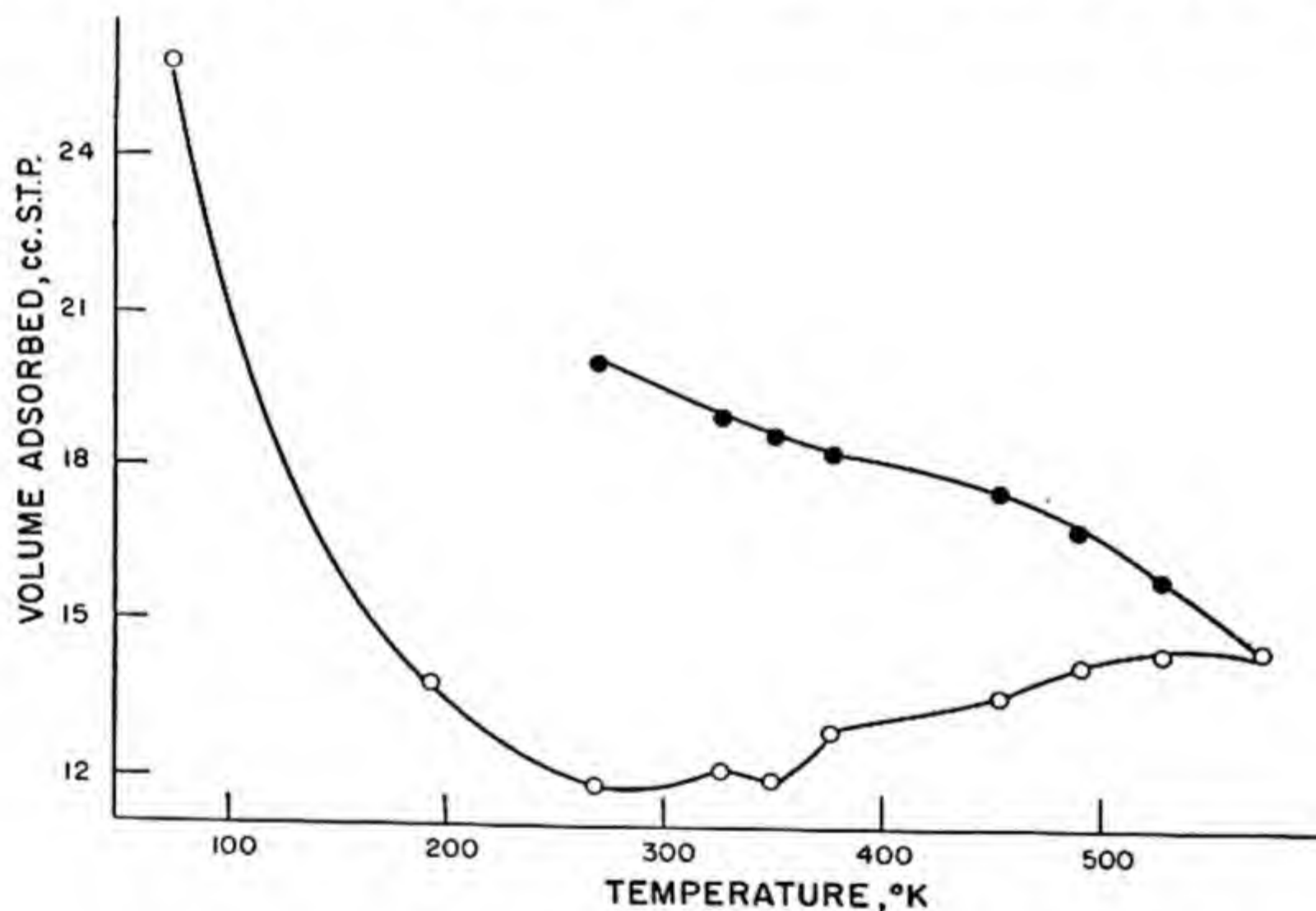


FIG. 14. H_2 Adsorption isobar on $\text{Ni}-\text{Cr}_2\text{O}_3$. $V_m = 36.38$ cc.

first that this catalyst exhibits chemisorption of hydrogen only in the temperature range above 0°C . It is more like a chromium oxide gel catalyst than the nickel catalysts already considered. It reveals, in the form of the curve obtained on lowering the temperature from 302 to 0°C ., that extensive desorption-readsorption occurs in this temperature range when the system is subjected to the technique of raising the temperature. The irregular form of the rising-temperature curve is further evidence of this. The large quantities of gas adsorbed at liquid nitrogen and dry ice

temperatures in terms of the nitrogen monolayer suggest, however, that some of this adsorbed gas is chemisorbed and at a rapid rate. There appear to be in this catalyst at least two main temperature ranges where hydrogen is chemisorbed, below -78°C . and above 0°C ., a definite index of wide variations in activity of the catalyst for chemisorption.

IV. EVIDENCE FROM THE EARLIER LITERATURE

1. Nickel

Two sharply differentiated types of active center for chemisorption of hydrogen on nickel were revealed by calorimetric and desorption studies conducted by Eucken and Hunsmann (15). The differentiation between van der Waals and chemisorption by means of calorimetric data was made convincing by calorimetric measurement of the heat of adsorption at temperatures from 20 to 195°K . At 20°K . physical adsorption only was observed with a mean heat of adsorption of 800 calories/mole. At 55°K . the adsorption was, in part, chemisorption since the observed heat of adsorption was somewhat less than 5 kcal./mole. At the three temperatures 90, 195 and 273°K . where the first quantities of gas were adsorbed with approximately the same heats of adsorption, in the neighborhood of 20 kcal./mole the gas appears to be completely chemisorbed. The catalyst was prepared by ignition of the nitrate to oxide and was carefully reduced in hydrogen at 300°C . for 4 days. It would appear to be more active for chemisorption than the preparations discussed in the preceding sections judged by the low temperature, 55°K ., at which chemisorption was calorimetrically evident. On the other hand, the authors' statement that a 50-g. filling of nickel in the calorimeter absorbed only 40 cc. hydrogen at 0°C . would be indicative of a low adsorption capacity in terms of the preceding data where adsorption at 0°C . and 1 atmosphere pressure attained, in the case of nickel-kieselguhr, 19.6 cc./g., and with the nickel-2% thoria reached 1.4 cc./g.

The desorption technique devised by Eucken and Hunsmann consisted in saturating the nickel preparation with a quantity of hydrogen, rapidly pumping off the dead space and easily desorbable gas at temperature, and then heating the preparation for 1-5 hours up to 600°K . with continuous evacuation. At regular intervals the temperature and hydrogen pressure over the nickel were observed and recorded. The data show that with adsorption at 195 and 273°K . there are two stages of desorption, one practically complete at 273°K ., the other first measurable at 473°K . The first stage involved 14% of the gas, the remainder being desorbed at the higher temperature. The gas adsorbed at 20°K . could be desorbed completely at slightly higher temperatures than 20°K . Also with adsorption

at 83° K. the adsorption was practically completely reversible at temperature so that the authors decided that it was not conclusive that there was a conversion at this temperature from physical to chemisorption. Nevertheless, the calorimetric data are decisive that at 90° K. the gas is chemisorbed. The conclusion seems compelling that the energy of desorption of hydrogen chemisorbed at 83° K. is markedly less than the energy of desorption of hydrogen chemisorbed at 195 and 273° K., again evidence for the heterogeneity of catalyst surfaces for chemisorption. Eucken and Hunsmann, from their calculated energies of desorption and their measurements of heats of adsorption, constructed a chart for the distribution of active centers over their nickel catalyst surface. Their graph is reproduced in Fig. 15. The horizontal lines indicate the areas which are covered by adsorption at the temperatures 90, 195, and 273° K. These are determined by the activation energies of adsorption, measured by $E_d - \Delta H_a$, where E_d is the activation energy of desorption and ΔH_a is the heat of adsorption.

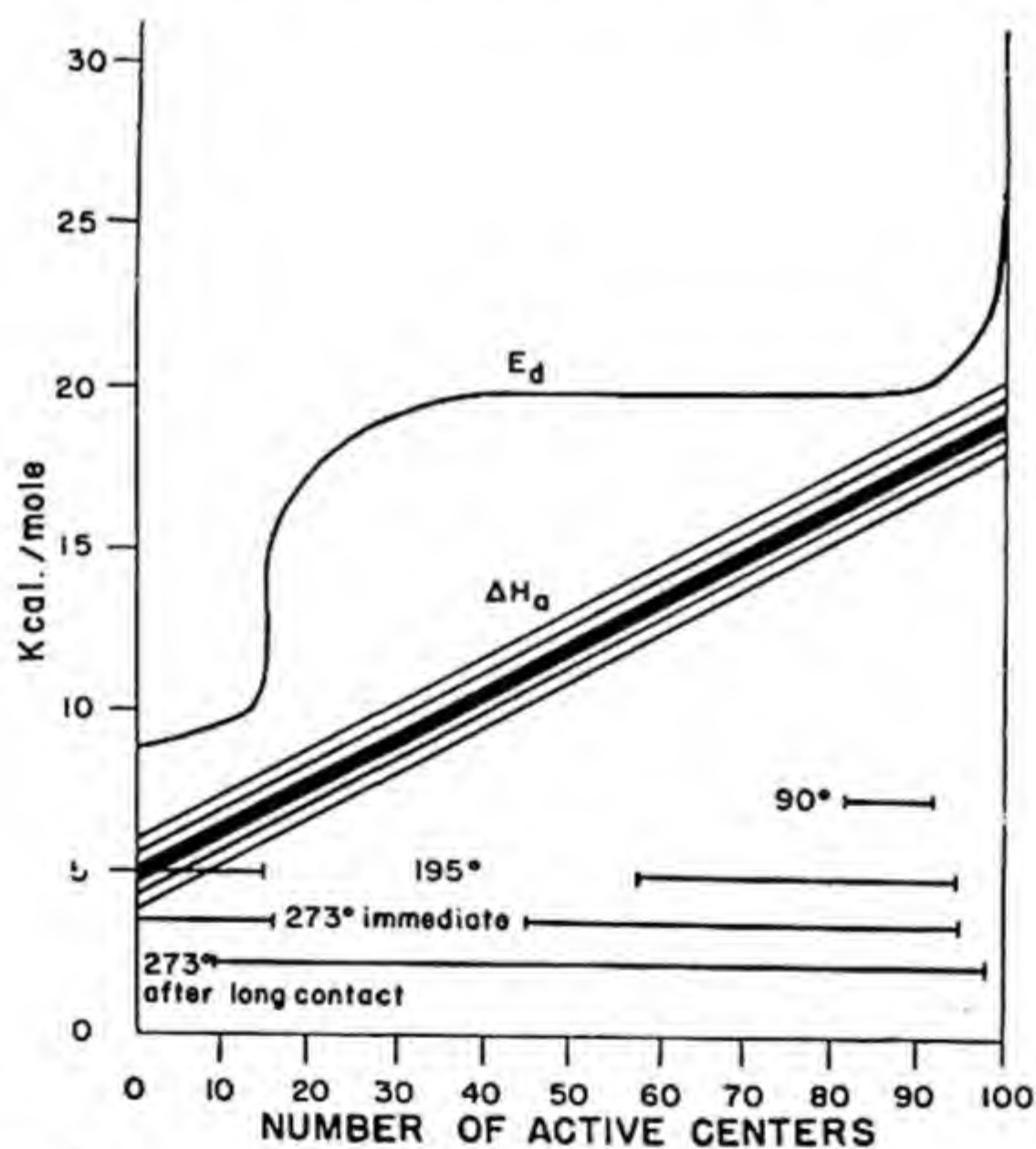


FIG. 15. Distribution of activation energy of desorption (E_d) and heat of adsorption ΔH_a , of the active spots on nickel surface. (The horizontal lines give the regions which become covered at the indicated temperatures.)

Special attention should be directed to the horizontal lines for 273° K. indicating immediate coverage and coverage after long contact. These are different. This arises firstly from the magnitude of the activation energies,

the areas of lowest activation energy being first covered. On standing, however, gas molecules are desorbed and readsorbed by unoccupied centers of higher heats of adsorption. It is in this fashion that Eucken and Huns-mann reach an explanation for an observed heat evolution in the calorimetric measurements after the adsorption of gas is complete. "The heat must in large part be due to a slow process which accompanies the adsorption and is not demonstrable manometrically." This is undoubtedly the process of desorption and readsorption occurring at a single temperature which is so very pronounced in the Princeton technique of raising the temperature at constant pressure. It could only arise with a surface having heterogeneous character.*

2. Iron Synthetic Ammonia Catalysts

Brunauer and Emmett (10) in their careful studies of iron catalysts had already observed (see especially Tables IV, X and XIII of the paper cited) the phenomenon of increasing adsorption with decreasing temperature that we have indicated as occurring in our studies, as recorded in Fig. 8, on other preparations of synthetic ammonia catalysts.

3. Tungsten

In the studies of hydrogen and nitrogen adsorption on tungsten powders Frankenburg and his associates (16) established the fact that the adsorption of nitrogen on tungsten increased with increasing temperature, that the establishment of equilibrium was a slow process and that, on cooling the system, the amounts taken up on increasing the temperature are not given off again. In a footnote (see reference 4 of the paper cited), in the article by Messner and Frankenburg (16a) there is recorded an observation essentially the same as that investigated in detail by Taylor and Liang. With a tungsten powder which had come to pressure constancy with nitrogen at a given temperature it was found that "after rapid temperature rise there is first a rapid increase in pressure, which is followed by a considerably slower decrease in pressure; the latter finally considerably outweighs the primary pressure increase." The authors follow this with the

* Throughout this paper the stress has been laid on the heterogeneity of the catalyst surfaces under study. Some workers in the field would assign the heterogeneity to a variation in the geometrical arrangement of the adsorbed molecules on the surface. From this point of view it might be of greater generality to speak of the heterogeneity of the surface-adsorption complexes. We believe, however, that new chemisorption data on a variety of surfaces, notably the measurements of Frankenburg (*J. Am. Chem. Soc.*, **66**, 1827, 1838 (1944)) of hydrogen on tungsten surfaces in which there is a linear relation between $\log \theta$ and $\log p$, θ being the fraction of the surface covered, cannot be explained by interactions between adsorbed molecules. They demand a heterogeneity of adsorption sites (see, for example, Halsey and Taylor, *J. Chem. Phys.*, **15**, 624 (1947)).

remark: "according to our view these two pressure effects correspond to a desorption and subsequent chemical binding." The data do not permit an estimate as to what extent the desorption occurring was of van der Waals' or chemisorbed nitrogen. If the latter, the evidence is direct that the tungsten surface is heterogeneous for nitrogen adsorption.

4. Chromium Oxide Gel

In a study of the effect of gas pressure on the chemisorption of hydrogen on chromium oxide gel, Taylor and Burwell (6f) found it necessary to resort to an arbitrary process of subtraction from experimentally observed amounts of adsorbed gas in order to display a relatively uniform area of gel for hydrogen chemisorption. Within close limits, at temperatures of 457 and 491° K. and at pressures of 1, 0.5 and 0.25 atmospheres, the energy of activation for the adsorption process was nearly independent of the amounts of adsorption (0–35 cc.) and the activation energy was about 21 kcal. In the temperature range 383 to 457° K. no such uniformity was observed. For example, if the amounts adsorbed with time at 405 and 427° K. be used to calculate activation energies the values received increase from 0 to 18.5 kcal. as the amount of gas adsorbed on the surface increases from 1.6 to 8.5 cc. Similar results can be drawn from the earlier measurements of Kohlschutter (17).

As Burwell and Taylor observed, "the data as a whole appear to reveal (a) at higher temperatures, an activated adsorption with an activation energy and a pressure effect nearly independent of the amount of hydrogen adsorbed; and (b) at somewhat lower temperatures, an activation energy and a pressure effect varying markedly with the amount adsorbed.

"That any one definite process could be so changed in nature by a rather small change in temperature would be surprising. We will attempt to show that the deviation is but an apparent one, resulting not from a change in the nature of the higher temperature activated adsorption but from the increasing importance at lower temperatures of a process nearly negligible at higher temperatures.

"It will be assumed that some process causes the observed adsorptions throughout the greater part of the time-adsorption curve to exceed the adsorptions properly attributable to an adsorption with an activation energy of the order of 21 kcal. by the following amounts at the different temperatures and pressures" (see Table I).

They go on to suggest that "the amounts of gas which we have been led to subtract from the observed data in the lower temperature range, 383.5–457° K., represent activated adsorption occurring with lower activation energies than that characterizing substantially all the adsorption above 457° K. Since the amounts subtracted (see Table I) diminish with increas-

TABLE I
Arbitrary Deductions From Observed Adsorptions

Temp., ° K.	1 Atm.	Volumes, cc. 0.5 atm.	0.25 Atm.
383.5	3.15
405	2.5	1.6	1.05
427	1.65	1.15	0.75
457	1.15	0.65	0.45

ing temperature and decreasing pressure, and since only those sections of the curves after the eight, forty, and one hundred and fifty-minute abscissas at 427, 405 and 383.5° K., respectively, are utilizable, we conclude that the subtractions approximate to the equilibrium values of the adsorptions with lower activation energies at the pressures and temperatures indicated." The authors calculated that the heat of adsorption involved was of the order of 10 kcal./mole in contrast with a heat for the higher temperature adsorption of 27 kcal./mole. The desorption-readsorption observations of Taylor and Liang are confirmatory of this early interpretation of heterogeneity in chromium oxide gel surfaces.

Beebe and Dowden (18) measured the heat of adsorption of hydrogen on chromium oxide gel at liquid air temperatures. They found a heat of adsorption of 5 kcal./mole which is larger than that to be expected for van der Waals adsorption. This gas, however, with the low energy of activation allowable at liquid air temperature cannot be held to the surface in the temperature range 457 to 491° K. where chemisorption with an activation energy of 21.7 kcal. "on an area relatively uniform and large in extent" is occurring.

5. Zinc-Chromium Oxide

As early as 1930 Garner and Kingman (19) reported that hydrogen adsorbed at room temperatures and low pressures on ZnO-Cr₂O₃ catalysts was given off at 100–120° but after 20 to 30 minutes was readsorbed. At the time of these experiments it was not possible to state whether the gas adsorbed at room temperatures was van der Waals or chemisorbed gas. The later work by Liang definitely indicates that chemisorbed gas undergoes desorption and readsorption on such catalysts in the temperature region in question.

6. Zinc Oxide

The heterogeneity of zinc oxide catalysts as revealed in the recent work of Taylor and Liang serves to confirm the conclusions of Taylor and

Smith (6g) reached by study of the velocity of interaction of H_2 and D_2 at temperatures between 143 and $491^\circ K$. In that research it was shown that the catalyst operated in that temperature range with activation energies which increased from 0.6 kcal. in the temperature range $143-178^\circ K$. through a region $195-373^\circ K$. with an activation energy of 7 kcal. to a high temperature region with an activation energy of 12 kcal. In this latter there was a temperature range in which the apparent activation energy was zero. This latter abnormality was interpreted on the basis of a decrease in active surface covered with increase of temperature. A further observation of Taylor and Smith is pertinent. The velocities of the exchange reaction were occurring from 50 to 800 times faster than the net rate of adsorption of hydrogen at atmospheric pressure, as measured by Strother on material of similar mode of preparation.

The argument developed by Taylor and Smith was based on the postulate that the slow step in the exchange reaction was a desorption of chemisorbed hydrogen deuteride from the zinc oxide surface. Since this was occurring many times faster than the observed adsorption of hydrogen at a given temperature and pressure it would follow that the desorption process was occurring on an area of the surface where the activation energy of *desorption* was less than the activation energy of the adsorption process occurring under the specified conditions of temperature and pressure. Two different areas of the surface were therefore involved, at a given temperature, in the exchange reaction and the adsorption process. The postulate of Taylor and Smith was challenged by others (20, 21) who were engaged on similar exchange studies on metal surfaces. These authors postulated a mechanism involving interaction between an impinging molecule and a chemisorbed atom attached to the surface. With this alternative postulate the argument of Taylor and Smith in favor of heterogeneity of surface could thus be discounted. The data of Taylor and Liang which reveal the heterogeneity of such zinc oxide surfaces by experimental observations entirely free from any postulate with respect to reaction mechanism tend to strengthen the conclusions derived from the earlier experiments on exchange reaction.

The great advantage of the study of exchange reactions of isotopic molecules on catalysts is that only one molecular species is involved both as reactants and products. One is freed from the restrictions imposed with two reactants where the displacement of one reactant by another or by a reaction product must steadily be taken into consideration. The catalysts which reveal heterogeneity by desorption-readsorption studies should show the same variation in activation energy of reaction with temperature that Taylor and Smith found with zinc oxide in the hydrogen-deuterium reaction. Research in this direction is under way.

V. GENERAL OBSERVATIONS

The heterogeneity of catalyst surfaces displayed in the desorption-readsorption phenomena already detailed and in the reaction of isotopic molecules must be equally a factor in all catalytic reactions to a greater or less degree, dependent on the type of reaction and also the extent to which one or another reactant or product determines the reaction mechanism. In analyzing the process in any particular case it will be necessary to determine to what extent the total accessible surface, determined for example by the B.E.T. technique, is involved in the rate-determining slow process of the overall sequence. Thus, in the case of ammonia synthesis, where the activation of nitrogen is clearly the rate-controlling factor, it has further to be determined what fraction of the total accessible surface can play a role in such activation under a prescribed set of conditions. If similar conditions prevailed with nitrogen on synthetic ammonia catalysts as obtained with hydrogen on several of the catalyst surfaces here discussed then it would follow that only certain fractions of the total accessible surface could be effective in a given temperature-pressure operation, and these could well be different in other reaction conditions.

A further observation is pertinent. The present analysis forces the conclusion that, at a prescribed condition of temperature and pressure, the slow processes of chemisorption or interaction with the surface by a reactant that can be demonstrated and measured at such a condition can have little significance in a rapid catalytic reaction that may occur under the condition specified. It is the processes of rapidly occurring desorption which are significant. To this extent the measurements of slow processes of chemisorption are not significant for catalytic reactions occurring rapidly at the given temperature and pressure. They may well be significant for catalytic actions at higher temperatures. For example, the slow process of interaction of carbon monoxide with Fischer-Tropsch catalysts to yield carbided catalysts, and measured in their progress over hours of observation, can have little significance in the catalytic synthesis of hydrocarbons which occurs at the same temperatures in time intervals of the order of seconds. It may well be, however, that the demonstrated rapid interactions which occur in the first moments of interaction of carbon monoxide with the catalyst do possess significance. The nature of the interaction cannot readily be studied at such a temperature owing to the rapidity of the interaction. Its occurrence in measurable time intervals at a lower temperature may well have significance for the catalytic reaction at the higher temperature.

Finally, it should be obvious that the variations in quality of surface that these studies of a particular group of catalysts have revealed go far to elucidating the variations in catalytic behavior of a catalyst that are com-

mon on examination, by different workers, of a particular mode of preparation of the catalyst. It is apparent that small variations in operational techniques can produce relatively large variations in the distribution of centers of activity. Indeed, variability in performance of catalysts produced from a given set of operations may well be the index of a pronounced heterogeneity of surface.

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Alkylation of Isoparaffins

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I. INTRODUCTION

1. Historical

The catalytic alkylation of saturated hydrocarbons with olefins was discovered and developed by Ipatieff and his co-workers in the laboratories of the Universal Oil Products Company (Ipatieff, 1). Experiments were carried out in June, 1932, by Ipatieff and Pines, using aluminum chloride as the catalyst, hydrogen chloride as a promoter, and hexane and ethylene as the reactants. These experiments having given positive results, they were repeated by Komarewsky, who then also investigated the alkylation of naphthenes. The alkylation of hexane was studied quantitatively by Grosse, who extended the reaction to other paraffins and catalysts, particularly boron fluoride.

Intensive research on catalytic alkylation of paraffins resulted in a number of commercial processes for the production of high octane number motor fuel from refinery gases. The reaction played a major role in World War II, for it provided the means of producing "alkylate," an important component of 100-octane aviation gasoline. For this purpose it had advantages over the alternative process involving olefin polymerization followed by hydrogenation because it yielded an isoparaffinic gasoline directly and because it permitted the utilization of butanes as well as of olefins, thus yielding approximately twice as much gasoline from a given amount of olefin. Alkylate was produced at the rate of over five million gallons a day during the war.

2. Scope

Only the results presented in papers appearing in the scientific chemical literature will be discussed. Papers dealing with the technical modifications and engineering features necessary for the successful industrial application of the alkylation reaction to the production of gasoline are outside the scope of this article. Also, none of the more than seven hundred and fifty United States patents which relate to alkylation processes or to catalysts for them is to be considered here.

It is the object of this review to present a critical discussion of the catalytic alkylation of isoparaffins and of the reaction mechanism. A comprehensive and detailed summary of the papers which had been published on this subject up to the middle of 1945, appeared in *Chemical Reviews* (Egloff and Hulla, 2).

3. Preliminary Survey

The alkylation of paraffins with olefins to yield higher molecular weight branched-chain paraffins may be carried out thermally or catalytically. The catalysts for the reaction fall into two principal classes, both of which may be referred to as acid-acting catalysts: (1) anhydrous halides of the Friedel-Crafts type and (2) acids. Representatives of the first type are aluminum chloride, aluminum bromide, zirconium chloride, and boron fluoride; gaseous hydrogen halides serve as promoters for these catalysts. The chief acid catalysts are concentrated sulfuric acid and liquid hydrogen fluoride. Catalytic alkylations are carried out under sufficient pressure to keep at least part of the reactants in the liquid phase.

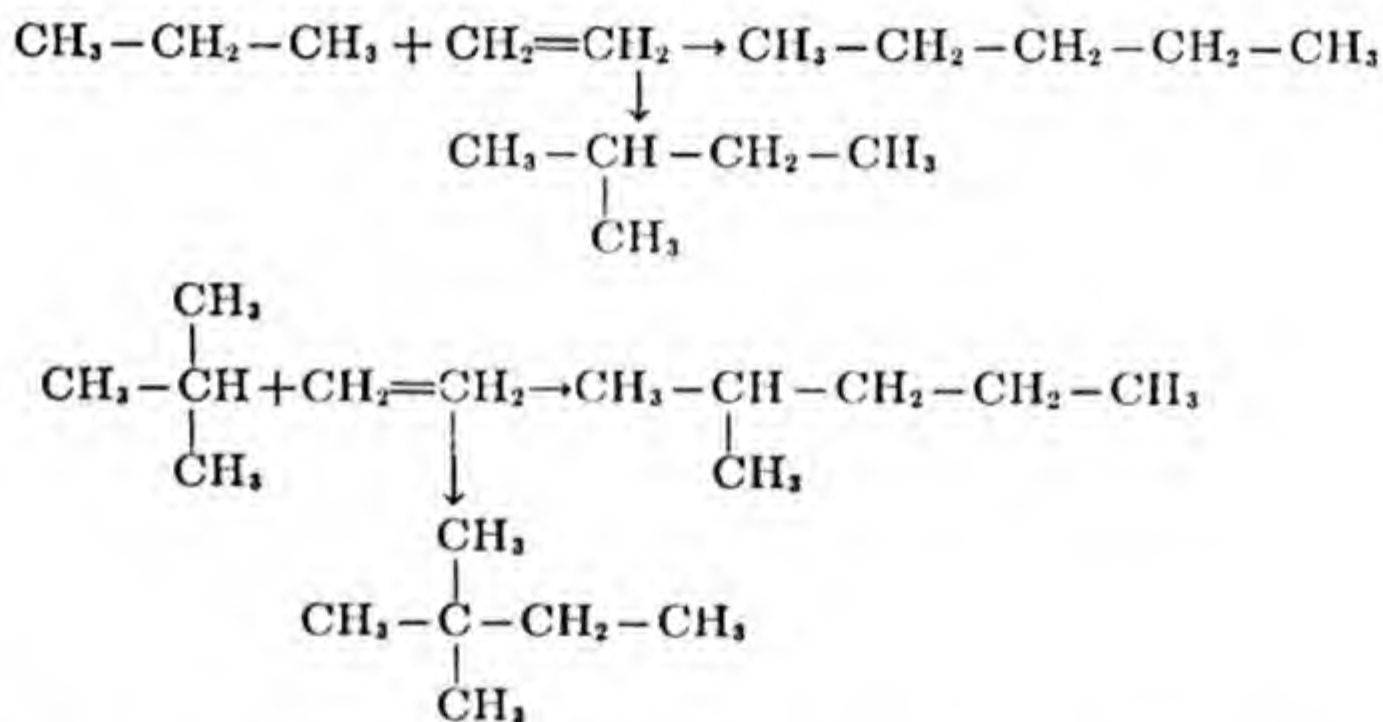
Propane and higher paraffins may be alkylated thermally. On the other hand, only paraffins which contain tertiary carbon atoms readily undergo catalytic alkylation. No method for the alkylation of methane and ethane in practical yield has been reported. The alkylation of isobutane has been most extensively investigated because the reaction converts this gaseous isoparaffin to liquid gasoline of high antiknock value.

Alkylation of isopentane, on the other hand, has been chiefly of academic interest since this isoalkane is already a liquid with a relatively high octane number.

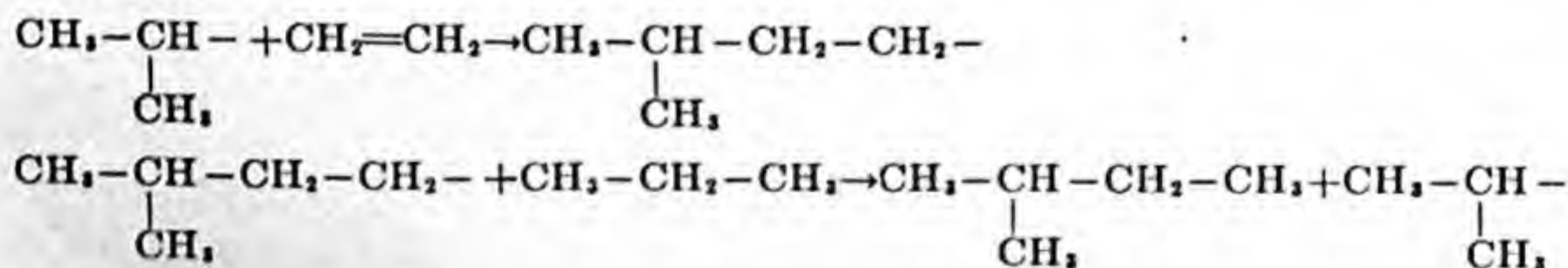
The gaseous olefins (ethylene, propylene, and the butylenes) are the preferred alkylating agents. Low ratios of olefin to isoparaffin are used in order to minimize or prevent polymerization of the olefin. Mole ratios of 1 to 3 or 4 are usually employed in the laboratory; ratios as low as 1 to 8 or even lower are not uncommon in commercial alkylations.

a. Thermal Alkylation. The noncatalytic alkylation of paraffins will be given brief mention here primarily for purposes of comparison. Such alkylation requires high temperatures (about 500°) and pressures (about 2500 to 4500 p.s.i.). The main products of the reaction of ethylene with propane and isobutane, respectively, are pentanes and hexanes (Frey and Hepp, 3; Oberfell and Frey, 4).

The reaction takes place by the addition of an alkyl group and a hydrogen atom derived from the alkane to the double bond of the olefin:



A free radical chain mechanism is probably involved. Thus, for example,



Since tertiary alkyl radicals are formed more readily than primary, it is to be expected that more isopentane than *n*-pentane will be obtained by the alkylation of propane, and more neohexane than isohexane will be produced from isobutane. The experimental results show this to be the case.

For example, the reaction of propane with ethylene at 510° and 4500 p.s.i. pressure resulted in a liquid product containing 55.5% by weight isopentane and 16.4% *n*-pentane, 7.3% hexanes and 10.1% heptanes; 7.4% alkenes were also present. The formation of alkenes and other by-products indicates that thermal cracking occurred. The alkylation of isobutane with ethylene under the same conditions yielded a liquid product containing 44.3% by weight neohexane, 11.6% isohexane, 1.1% *n*-hexane, 4.5% heptanes, 9.6% octanes as well as minor amounts of other alkanes and alkenes. This reaction has served as a means for producing neohexane commercially.

Thermal alkylation occurs readily with ethylene, less readily with propene and *n*-butylenes, and with difficulty with isobutylene. (As will be shown, the reverse is true in catalytic alkylation.) The reaction of propane with propene at 505° and 6300 p.s.i. yielded a liquid product containing 18.0% 2,3-dimethylbutane, 17.7% 2-methylpentane, and 5.4% *n*-hexane. An even higher pressure, 8000 p.s.i. was required for the reaction of isobutylene with isobutane at 486°; the liquid product, whose yield was only 10–20% of that obtained when ethylene was used, contained 34.0% octanes but also 32.7% octenes.

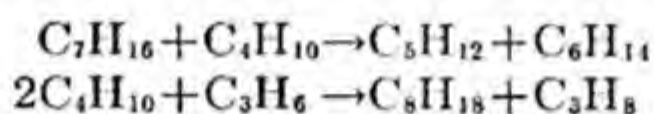
It has recently been shown that the alkylation takes place under milder conditions if a small amount (1–3% by weight of the total charge) of a halogen-, nitrogen-, or oxygen-containing compound is added to the mixture of paraffin and olefins (O'Kelly and Sachanen, 5). Suitable "homogeneous catalysts" included chloroform, benzyl chloride, benzal chloride, acetyl chloride, trichloroacetaldehyde, nitromethane, and tribromopropane. Both normal and branched chain paraffins were alkylated. Reaction occurred at 300–400° at pressures of about 3000 p.s.i. or higher. For example, the continuous alkylation of isobutane with ethylene at 427° and 2500–3000 p.s.i. pressure, in the presence of 1% by weight of a chlorinated naphtha, resulted in alkylate to the extent of 190% by weight of the ethylene charged. The hexane fraction (43% of the alkylate) consisted mostly of neohexane, which was thus obtained in about 25% of the theoretical yield. Formation of neohexane appears to indicate that the free radical mechanism is again involved, the "catalysts" serving as chain-initiators.

b. Catalytic Alkylation. The catalytic alkylation of isoparaffins takes place at very much lower temperatures and pressures than does the thermal reaction. Yields are usually higher. Depending on the particular reactants and catalyst used, the temperature may be as low as –30° or as high as 100°. The pressure is usually the vapor pressure of the reaction mixture and ranges from 1 to 15 atmospheres. Alkylation with ethylene takes place more readily in the presence of the metal halide catalysts than in the

presence of the acid catalysts. All of the catalysts are converted to addition complexes (so-called "lower layer" or "sludge") with highly unsaturated compounds formed during the reaction.

The products obtained by the condensation of isobutane with various olefins are not those to be expected from the simple addition of *t*-butyl and hydrogen across the olefinic double bond. Alkylation with ethylene yields 2,3-dimethylbutane and not 2,2-dimethylbutane, which is the product of the thermal reaction. Similarly, alkylation with propene yields 2,3- and 2,4-dimethylpentane rather than 2,2-dimethylpentane. The principal alkylation products from 1-butene (especially in the presence of aluminum chloride modified by reaction with methanol) are dimethylhexanes whereas those from 2-butene are trimethylpentanes.

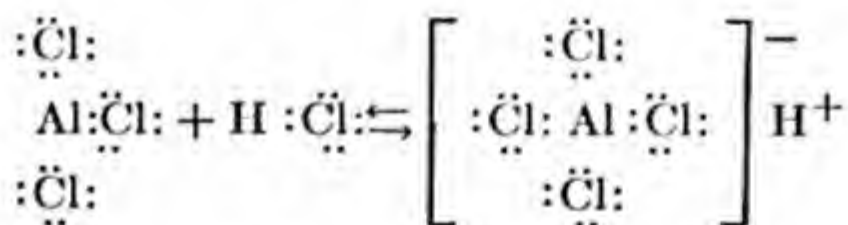
By-product formation is due chiefly to two side reactions, namely "destructive alkylation" and a hydrogen-transfer reaction, the net result of which is the hydrogenation of alkene and the "self-condensation" of the isoalkane.



The significance of these side reactions is discussed below in greater detail.

Catalytic alkylation of *n*-alkanes takes place only very slowly, particularly if conditions are not favorable for isomerization; side reactions often predominate.

(1) Halide catalysts of the Friedel-Crafts type. The most important catalysts of this class are anhydrous aluminum chloride and boron fluoride promoted by small amounts of hydrogen chloride and hydrogen fluoride, respectively. It has been suggested that a function of the hydrogen halide is to convert the aluminum or boron halide to a more active acidic form. For example:



Recent work (Brown and Pearsall, 6) has indicated that the hydrogen aluminum tetrachloride is nonexistent, but that interaction of aluminum chloride and hydrogen chloride does occur in the presence of substances (such as benzene and, presumably, olefins) to which basic properties may be ascribed. It has also been pointed out (Luder and Zuffanti, 7) that aluminum chloride and boron fluoride, being electron acceptors, are per se acids in the modern meaning of the word.

Modified aluminum chloride catalysts (aluminum chloride sludges, aluminum chloride monomethanolate, aluminum chloride-nitroalkane

solutions, and aluminum chloride-alkali metal chlorides) have been investigated with the view of overcoming certain disadvantages of the unmodified catalyst.

(2) Acid-type catalysts. Sulfuric acid of 96–98% concentration catalyzes the alkylation of isoparaffins with butenes and higher molecular weight olefins at 0–20°. Alkylation with propene requires acid of 98–100% concentration and a temperature of 30°. Alkylation with ethylene has not been very successful, presumably because stable ethyl hydrogen sulfate or diethyl sulfate forms too readily.

When liquid hydrogen fluoride is used as catalyst, alkylation may be accomplished in satisfactory yield (except with ethylene) at room temperatures. Higher temperatures can be used with hydrogen fluoride than with sulfuric acid because it is only with the latter that a side reaction, oxidation of the alkene, must be avoided.

Both sulfuric acid and hydrogen fluoride have found wide commercial use as catalysts for the alkylation of isobutane with propene and butenes.

II. THE MECHANISM OF THE CATALYTIC ALKYLATION OF PARAFFINS

As has already been mentioned, the catalytic alkylation of isoalkanes does not yield the anticipated isomers. Several mechanisms have been proposed to explain the formation of the products. The first of these (Ipatieff and Grosse, 8) postulated that the reaction proceeds via the addition of the *t*-alkyl group (corresponding to the isoalkane) and hydrogen to the olefin to yield a paraffin containing a quaternary carbon atom; this compound is not isolated but undergoes isomerization to form the isomeric alkane which is actually obtained. Thus, for example, the alkylation of isobutane with ethylene would yield 2,2-dimethylbutane as the unstable intermediate and 2,3-dimethylbutane as the final product. A serious objection to this mechanism is that 2,2-dimethylbutane is the predominant hexane in equilibrium mixtures of hexanes at temperatures up to 200° and even higher (Rossini, Prosen, and Pitzer, 9). Therefore, it is to be expected that if 2,2-dimethylbutane were formed as the primary product, only a small part would rearrange and a substantial amount would be present in the alkylation product.

A second mechanism (Birch and Dunstan, 10) differs from the first in that it proposes that the alkylation involves a primary rather than the tertiary carbon atom of the isoalkane. Alkylation of isobutane with propene, for example, would occur by addition of isobutyl and hydrogen to the double bond to yield 2,4-dimethylpentane. Isomerization of part of this heptane would then produce 2,3-dimethylpentane which is also a major product of the reaction. It was postulated that the isoparaffin is activated

(via the formation of a complex with the catalyst, sulfuric acid) and dissociates into a negative alkyl group (in this example, isobutyl) and a proton, the proton coming from a methyl group. The alkene is activated by addition of a proton, furnished by the acid, to form a positive alkyl ion (isopropyl). Combination of the carbanion and the carbonium ion yields the paraffinic product (2,4-dimethylpentane). However, this mechanism has the same objectionable feature as the first; the proposed isomerization of the primary product is improbable.

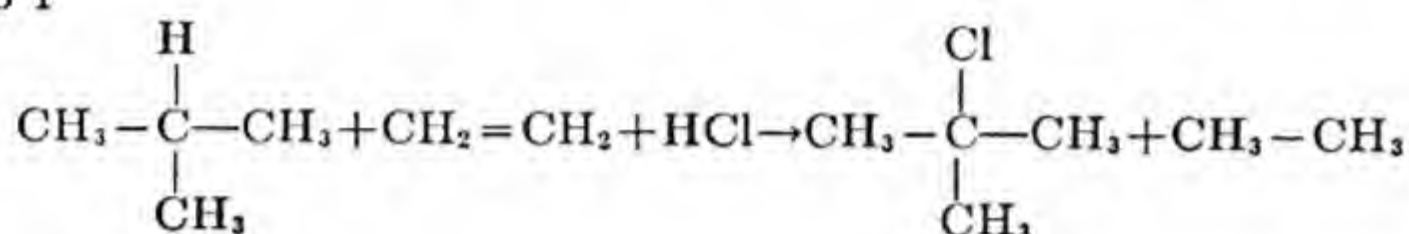
Two groups of investigators (Caesar and Francis, 11; McAllister *et al.*, 12) have proposed mechanisms which are similar in that each assumes that the isoparaffin undergoes carbon to carbon cleavage to yield two alkyl fragments (isopropyl and methyl, in the case of isobutane) which then add to the olefinic double bond to yield a higher molecular weight paraffin. The mechanisms do account for the structures of the products obtained. However, to explain the formation of 2,3-dimethylbutane by the alkylation of isobutane with ethylene, it is necessary to assume that the ethylene acts as if it were ethylidene. A similar postulation for the alkylation of isobutane with propene (i.e., isopropylidene) would lead to the erroneous conclusion that 2,2,3-trimethylbutane is formed in substantial amount.

A modified form of this mechanism has been proposed (Gorin, Kuhn, and Miles, 13). By assuming that the alkyl fragments (behaving as if positively and negatively charged) add to a complex formed between catalyst and olefin and by setting up rules governing the "preferred" form of the complex, it becomes possible for this type of mechanism to explain why some isomers are formed and others are not when isoparaffins are alkylated with olefins. However, this mechanism does not explain the formation of all of the products which are obtained when isoparaffins are condensed with chloroolefins (which may be considered to be "tagged" olefins) in the presence of aluminum chloride (Schmerling, 14b). Thus, for example, while it can explain the formation of 1-chloro-3,4-dimethylbutane by the reaction of isobutane with allyl chloride, it cannot explain the formation of 1,2-dichloro-4,4-dimethylpentane as a by-product of this reaction. Furthermore, it does not account for the principal chlorinated product of the reaction of isobutane with vinyl chloride (namely, 1,1-dichloro-3,3-dimethylbutane) or with 1,2-dichloroethylene (namely, 1,1,2-trichloro-3,3-dimethylbutane).

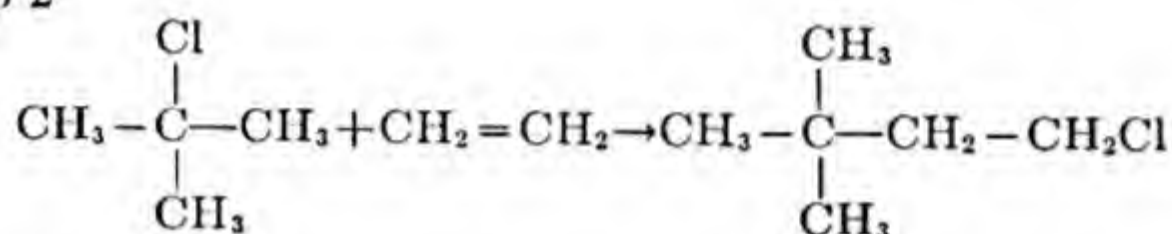
A mechanism which seems to give a truer picture of what occurs during alkylation (and which readily explains the formation of the polychloroalkanes as inherent products, see Section IV, 1c) proposes that the reaction is a chain reaction involving the conversion of the isoparaffin into a *t*-alkyl ester (Schmerling, 14). The alkylation of isobutane with ethylene is used below in illustration of this mechanism. Similar reactions occur with other

isoalkanes and alkenes. The separate occurrence of each step was proved rigidly only for aluminum chloride as catalyst. However, since the alkylation products obtained with other catalysts, including hydrogen fluoride and sulfuric acid, are similar to those obtained with aluminum chloride, it may be presumed that analogous reactions occur with these other catalysts, the reaction intermediates being *t*-alkyl fluorides and *t*-alkyl hydrogen sulfates, respectively, rather than *t*-alkyl chlorides.

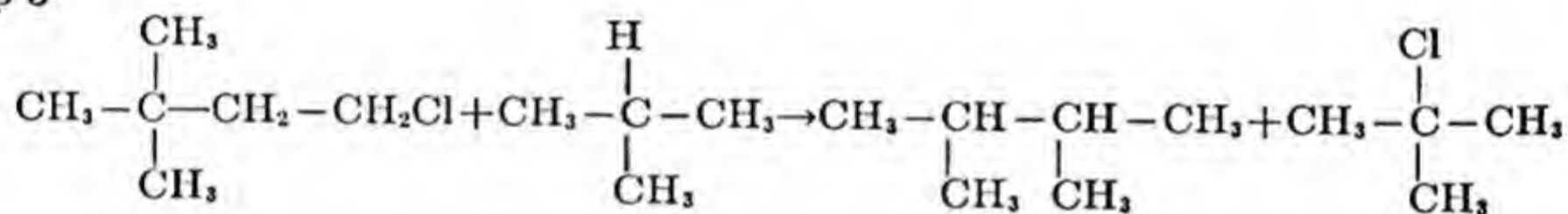
Step 1



Step 2



Step 3

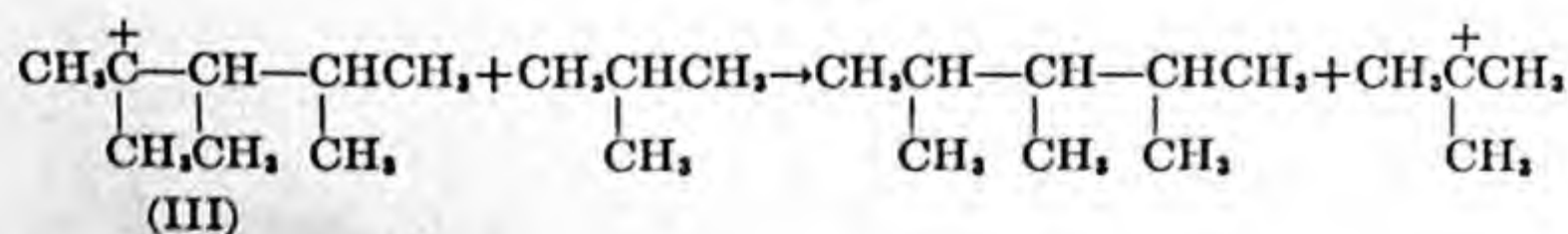
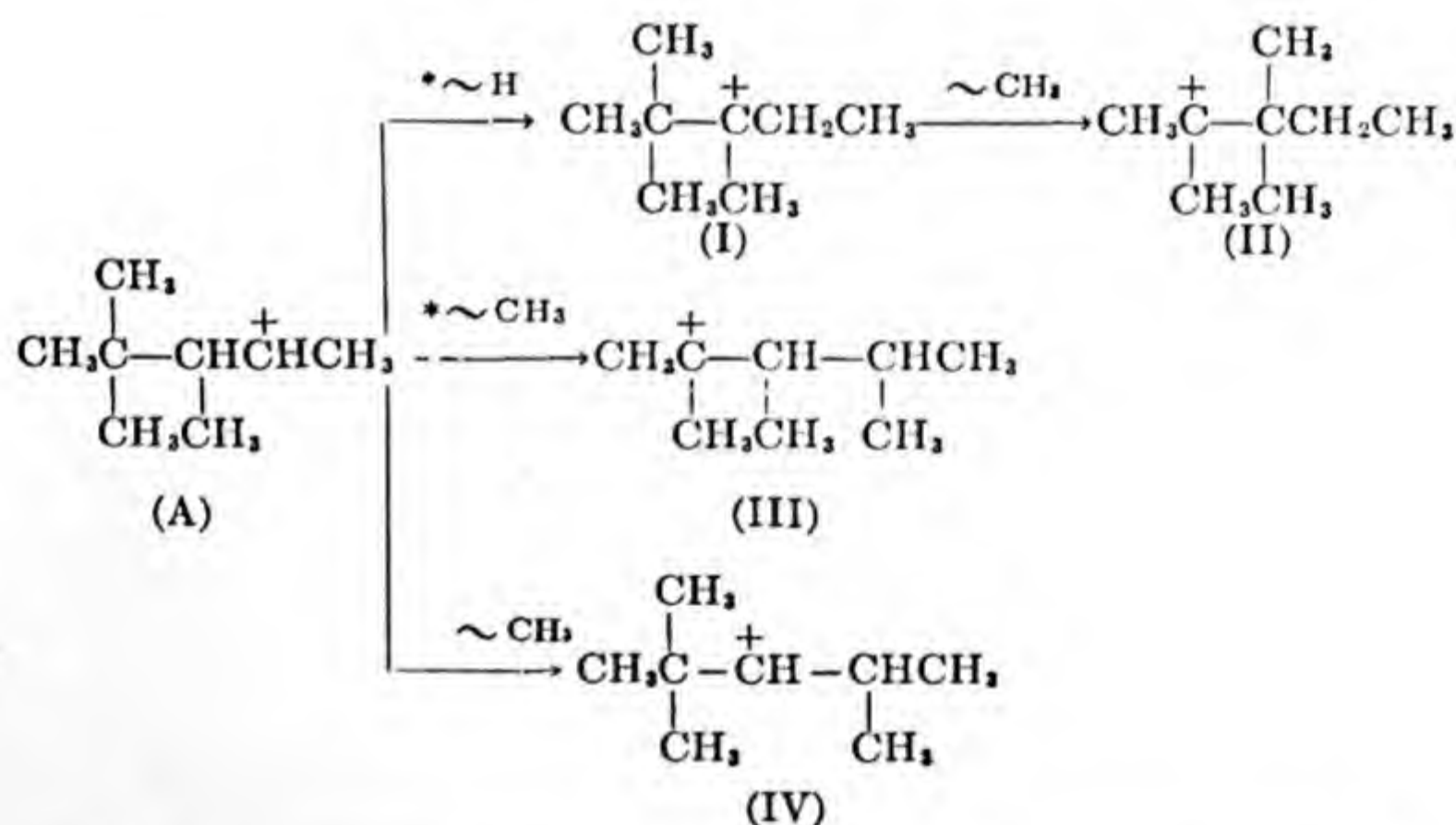
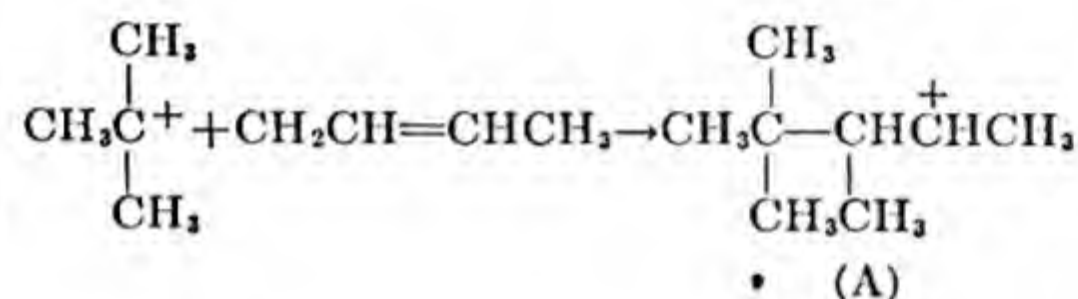
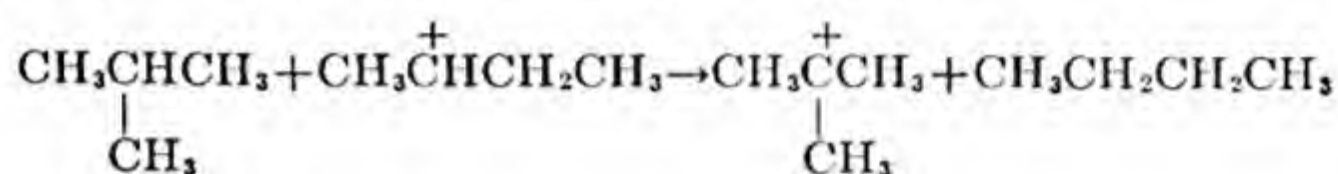
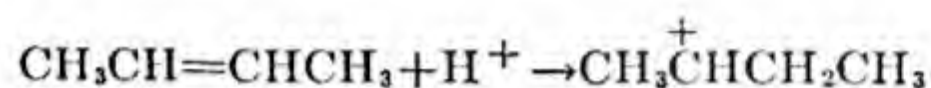


The *t*-butyl chloride formed in step 3 starts a new cycle by reacting with ethylene as in step 2. Ethane is produced only in the initiating step and the amount formed is, therefore, small.

Brief mention will be made here of only part of the considerable evidence which may be cited in support of each of the three steps. Thus, the first step (which probably occurs via the formation of ethyl chloride) finds confirmation in the fact that isoalkanes and alkyl halides undergo hydrogen-halogen exchange in the presence of aluminum chloride to yield *t*-alkyl halides and the alkanes corresponding to the original alkyl halides (Bartlett, Condon, and Schneider, 15). The primary reaction of *t*-alkyl chlorides with alkenes in the presence of aluminum chloride (i.e., step 2) is one of addition of the alkyl group and the halogen to the double bond of the alkene; a 75% yield of 1-chloro-3,3-dimethylbutane is obtained by the condensation of *t*-butyl chloride with ethylene at -10° in the presence of aluminum chloride (Schmerling, 16). The third step involves a hydrogen-halogen exchange similar to that of step 1, except that it is accompanied by skeletal rearrangement. Direct proof that rearrangement of the carbon skeleton of the alkyl chloride occurs during its conversion to alkane is the fact that 2,3-dimethylbutane and *t*-butyl chloride are major products of the reaction of 1-chloro-3, 3-dimethylbutane with isobutane in the presence of

aluminum chloride at room temperature; comparatively little 2,2-dimethylbutane is formed (Schmerling, 14c).

The rearrangement which occurs in step 3 may best be explained in terms of Whitmore's theory of intramolecular rearrangements (Whitmore, 17); the reactions of steps 1 and 2 may, of course, also be expressed in terms of "carbonium ions" (cf. Bartlett, Condon, and Schneider, 15). Thus, the alkylation of isobutane with 2-butene may be illustrated by the following equations (Schmerling, 14d):

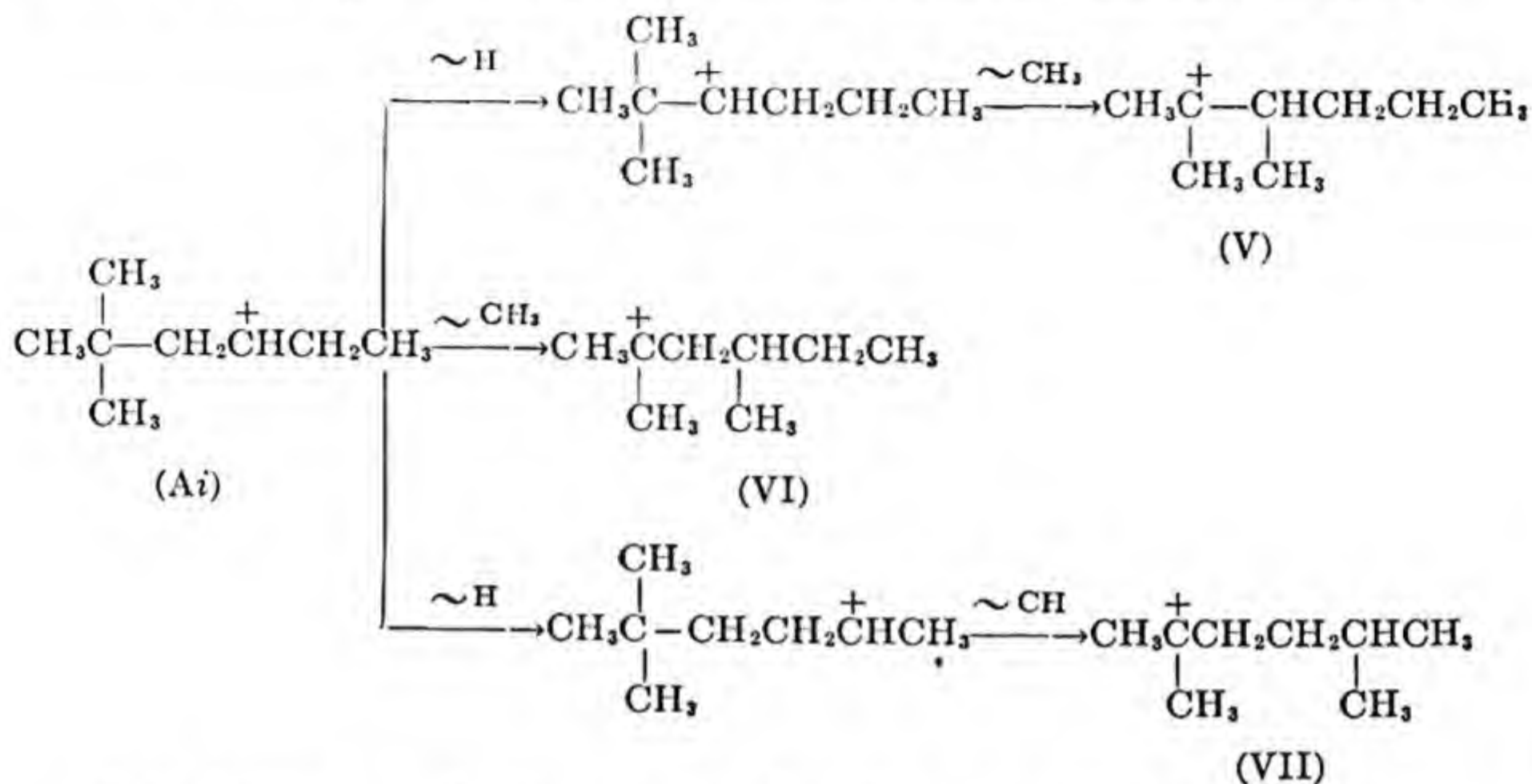


The other octyl ions (I, II, and IV) are similarly converted to the corresponding trimethylpentanes. Because relatively little 2,2,3-trimethyl-

*~ Signifies a shift in position of the CH₃ group or the H atom. Read as migration of the CH₃ group, or migration of the H atom.

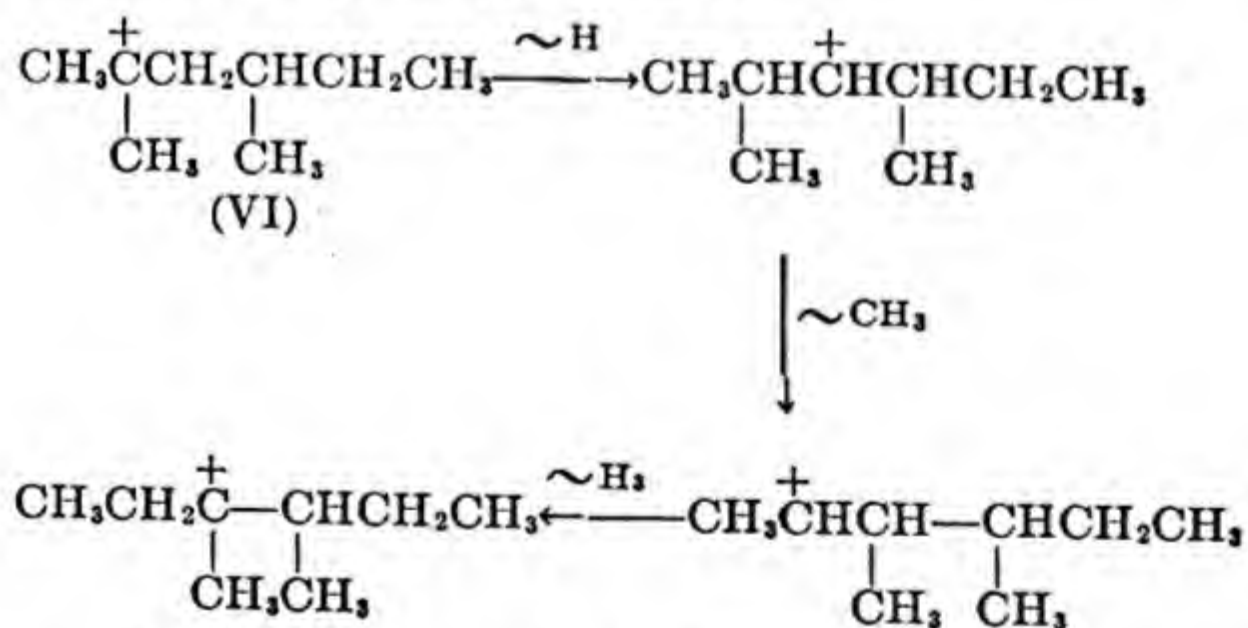
pentane is obtained, it may be concluded that (I) is quite unstable and rearranges to (II) very readily.

The alkylation of isobutane with 1-butene may be described by similar equations. The intermediate condensation product (A') which corresponds to the 2-butene product (A) undergoes the following rearrangements:



The tertiary carbonium ions (V), (VI) and (VII) are converted to dimethylhexanes by reaction with isobutane.

The formation of (VII) may involve several intermediate hydrogen and methyl migrations rather than the 1,4-shift shown. Similarly, the fact that 3,4-dimethylhexane is also a product of the alkylation indicates that the following changes occur:



Subsequent to the publication of the above discussed mechanism in condensed form, a partially similar mechanism was proposed (Ciapetta, 18). The point of similarity is that the latter assumes that a tertiary alkyl carbonium ion (or, in the molecular sense, ester) adds to the olefin to yield a carbonium ion of higher molecular weight which then undergoes carbon-

skeleton rearrangement before being converted to the paraffin product. A very important point of difference is that Ciapetta does not use a chain mechanism for the continued conversion of the isoparaffin to the carbonium ion and of the olefin addition product to the final paraffin. Instead, he postulates that the isoparaffin loses a proton from the tertiary carbon atom to yield a carbanion which then loses a pair of electrons to form the carbonium ion. In the final step, the proton and the electrons add to the carbonium ion of higher molecular weight, forming the paraffin product. The chain reaction scheme involved in steps 2 and 3 shown above appears to be preferable because it offers a more logical and plausible explanation for the conversion of the isoparaffin to the reactive tertiary alkyl chloride or carbonium ion; it is very highly improbable that free electrons can exist in a reaction mixture in the manner proposed by Ciapetta. Furthermore, if both carbanions and carbonium ions are formed, some of their interaction product (2,2,3,3-tetramethylbutane in the case of isobutane) should be obtained. No evidence of the presence of this octane in an alkylation product has been found. Also, this mechanism does not account for the dichloroalkanes formed by the reaction of isobutane with allyl or vinyl chloride.

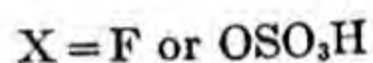
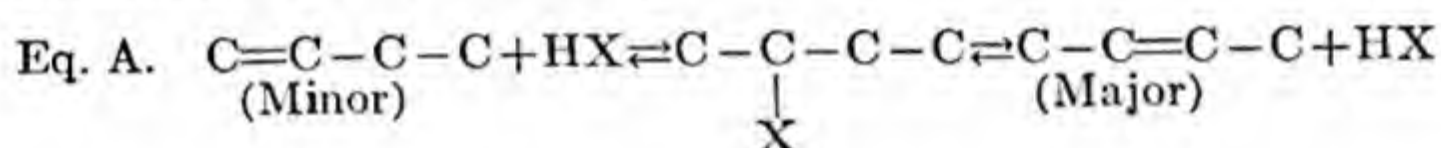
It follows from the above discussion that the chain mechanism requires that markedly different products be obtained in the alkylation of isobutane with 1- and 2-butene, respectively. The former should yield dimethylhexanes and the latter, trimethylpentanes, as the major products. Such has been shown (Schmerling, 14d) to be the case when aluminum chloride (particularly when modified to diminish side reactions) was employed as catalyst. The product of the alkylation with 1-butene in the presence of aluminum chloride monomethanolate contained about 60% by weight dimethylhexanes and 10% trimethylpentanes, whereas the 2-butene product contained 65% trimethylpentanes and only 4% dimethylhexanes. The difference in composition was apparent also in the A.S.T.M. octane numbers of the 125° end-point gasolines. That from 1-butene had an octane number of only 76.1; that from 2-butene, 94.1.

When, on the other hand, hydrogen fluoride is used as catalyst for the alkylation of isobutane, there is only a relatively small difference in the character of the products obtained with the two *n*-butylenes (Grosse and Linn, 19). The octane numbers of the 150° end-point gasolines prepared by the alkylation of isobutane with 1- and 2-butene, respectively, were 92.7 and 95.3. Furthermore, there was no significant difference in the composition of the respective products obtained by the alkylation of isobutane with *s*-butyl fluoride or with 2-butene in the presence of hydrogen fluoride (Linn, 20).

Similarly, alkylation of isobutane with 1- and 2-butene, respectively,

in the presence of 97% sulfuric acid yielded gasolines (185° end point) of 92.9 and 93.0 octane number (Birch *et al.*, 21a). It has further been stated (McAllister *et al.*, 12; cf. Birch *et al.*, 21a) that "the reaction products obtained from the normal butylenes are quite similar to those obtained from isobutylene except for the amount of light ends formed." Irreversible isomerization of 1-butene into an equilibrium mixture of 2-butene and isobutylene was assumed to occur prior to reaction with the isobutane. (It is not necessary to assume isomerization to isobutylene since the alkylates obtained with isobutylene and with 2-butene would consist largely of trimethylpentanes and, hence, would be quite similar).

The difference between the behavior of the metal halide catalyst and that of the acid catalysts is readily explained (Schmerling, 14d) by postulating that the reaction which occurs most rapidly when a mixture of isobutane and 1- or 2-butene comes in contact with liquid hydrogen fluoride or sulfuric acid, is the addition of the acid to the olefin to form *s*-butyl ester. There then exists in the reaction mass an equilibrium mixture which may be described by the following:



Octanes produced via the addition of *t*-butyl ester (from isobutane) to the butenes so formed will be the same regardless of what alkylating agent is used and the product will contain more trimethylpentanes than dimethylhexanes. If *all* of the alkylate were produced through the olefins formed as in eq. (A), all three alkylating agents (1-butene, 2-butene and *s*-butyl ester) would yield *identical* products. However, part of the alkylate in the case of the butenes is formed by the direct reaction of the *t*-butyl ester with the olefin before the olefin has reacted with the acid catalyst; this accounts for the small differences in composition.

With aluminum chloride catalysts, on the other hand, the reaction proceeds chiefly via the addition of *t*-butyl chloride to the original butene before more than a relatively minor portion of the latter can react with the hydrogen chloride promoter to yield *s*-butyl chloride. Therefore, the two *n*-butylenes yield very different alkylates.

Experimental evidence in support of the postulation for the reactions that occur in sulfuric acid (or hydrogen fluoride) may be found in a study of the alkylation of isobutane with 2-butene in the presence of tritium sulfuric acid at 10° (Stewart and Denham, 22). The results indicate that there was random distribution of hydrogen and tritium atoms in the olefin and the catalyst prior to alkylation. Also, when 2-butene was bubbled through tritium sulfuric acid at a rate such that there was little absorption,

hydrogen-tritium exchange occurred, demonstrating not only rapid exchange but also reversible absorption of the olefin in the acid. It was shown further that comparatively little exchange occurs when isobutane (and hence, alkylate) is treated with tritium sulfuric acid for a relatively long contact time (20 minutes).

The relative difficulty in alkylating normal paraffins is presumably due to the fact that the exchange reactions of step 1 and step 3 do not take place as easily with hydrogen atoms attached to secondary carbon atoms as with those attached to tertiary carbon atoms (cf. Bartlett, Condon, and Schneider, 15). Under the conditions required to obtain the hydrogen-halogen exchange reaction with normal paraffins, polymerization of the olefin (which may be considered to occur via a reaction similar to that of step 2) takes place very readily and becomes the predominant reaction.

The probable function of hydrogen halides as promoters for the metal halides and boron fluoride in the alkylation of isoparaffins seems to be to initiate and maintain the formation of *t*-alkyl halide by the reaction of step 1. Also, it may convert the metal halide to the more active form, such as, for example, hydrogen aluminum tetrachloride or an ester thereof.

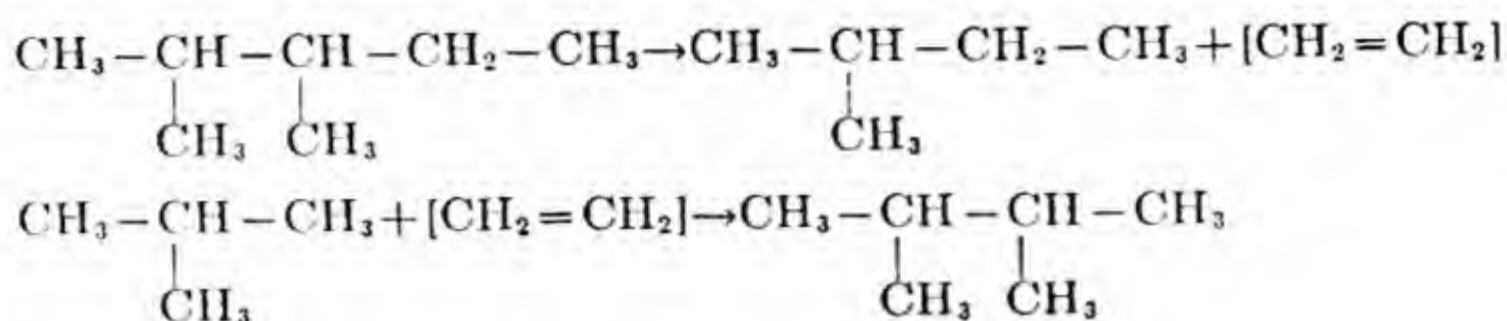
III. SIDE REACTIONS

1. *Destructive Alkylation*

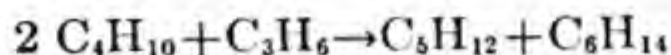
In virtually all cases, the alkylation of an isoparaffin with an olefin yields not only the products to be expected from the condensation of one molecule of the isoparaffin with one or more molecules of olefin but also paraffins of intermediate molecular weight. Thus, for example, pentanes, heptanes, and other alkanes containing an odd number of carbon atoms are obtained as by-products of the alkylation of isobutane with ethylene in the presence of aluminum chloride. Indeed, isopentane is usually formed in alkylation reactions involving isobutane regardless of the olefin or catalyst employed.

The formation of these by-products is apparently due in part to further reaction of the primary products by dissociation into "new" paraffins and olefins and the subsequent reaction of these olefins with the original isoparaffin (as well as of the "new" paraffins with original olefin). Such reactions, which may be termed "destructive alkylation," are similar to those which have been suggested to account for the products of the "autodestructive alkylation" of paraffins (Ipatieff and Grosse, 23).

By-product formation in the alkylation of isobutane with propene, for example, may be indicated as follows:



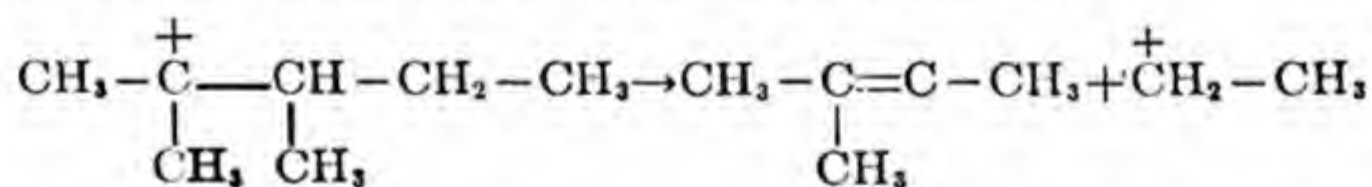
The over-all reaction may be written



It is apparent that the ratio of reacting isoparaffin to olefin may thus be greater than unity and the yield of alkylate based on the olefin may be higher than theoretical. Such high yields have been obtained in the alkylation of isopentane in the presence of sulfuric acid or hydrogen fluoride (see below).

In some cases, as in the alkylation of isobutane with ethylene, the destructive alkylation appears to involve the transfer of methylene.

The dissociation may be considered to be either a dealkylation or a depolymerization reaction. It presumably involves the intermediate formation of alkyl halide or other ester (or the corresponding carbonium ions) by hydrogen-halogen exchange followed by carbon-carbon cleavage. It has been pointed out (Bartlett, Condon, and Schneider, 15) that the criterion for ready cleavage of any carbonium ion is the possibility of forming a relatively stable smaller carbonium ion by cleavage between carbon atoms 2 and 3 (numbering from the carbon atom bearing the positive charge). Thus, during the alkylation of isobutane with propene,



The trimethylethylethylene may undergo polymerization, copolymerization, or alkylation, or it may add a proton and then be converted to isopentane by means of the hydrogen exchange reaction. The ethyl carbonium ion loses a proton to yield ethylene which may then react with isobutane (via *t*-butyl carbonium ion) to yield 2,3-dimethylbutane.

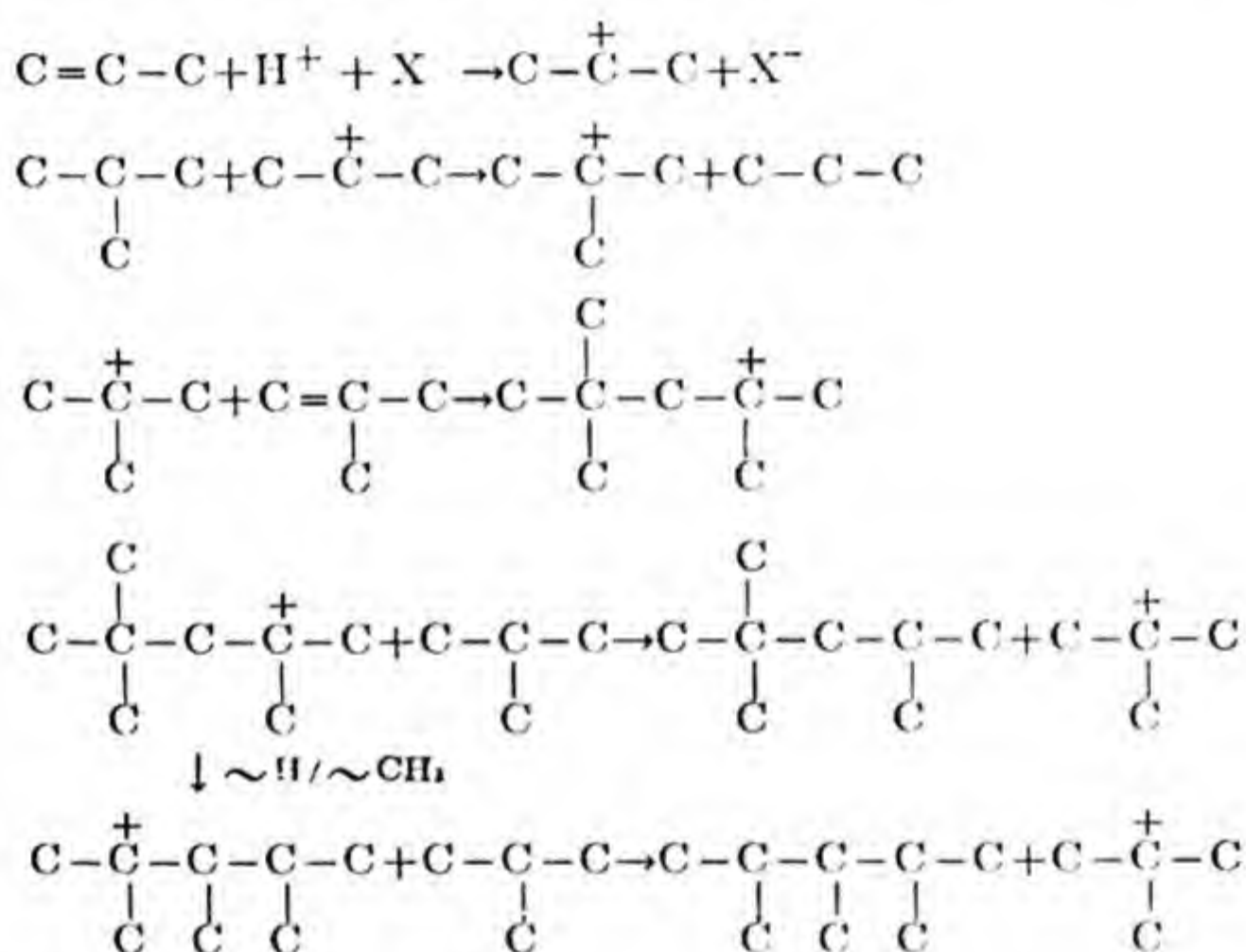
Insight into another mode of formation of these by-products is furnished by the observation that 1-chloro-3,3-dimethylpentane and 1-chloro-3,3-dimethylbutane are by-products of the condensation of ethylene with *t*-butyl chloride and *t*-amyl chloride, respectively, in the presence of aluminum chloride (Schmerling, 16). Partial conversion of either *t*-alkyl chloride into the other presumably occurs under the reaction conditions. It is apparent, then, that the alkyl chloride formed as indicated in step 3 of the three step chain mechanism may be converted into a chloride of higher or lower molecular weight before undergoing the condensation of

step 2, and that further reaction of the condensation product with isoparaffin yields the by-product paraffin and *t*-alkyl chloride in accordance with step 3.

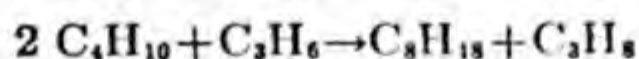
2. Hydrogen Transfer

Hydrogen transfer resulting in the conversion of more or less of the olefin to paraffin always accompanies the catalytic alkylation of isoparaaffins with olefins. At the same time, some of the isoparaaffin is converted to paraffin containing twice the number of carbon atoms; thus, for example, trimethylpentanes are formed in all isobutane alkylations regardless of the olefin used.

This side reaction may be explained (Schmerling, 14c, d) as follows in terms of the three step chain mechanism:



The over-all reaction may be written



It is obvious that the production of trimethylpentane involves the formation of an equimolar quantity of a low-boiling paraffin corresponding to the olefin alkylating agent. Such was found to be at least semiquantitatively the case. It will be noted also that 2 moles of isobutane are consumed for each mole of liquid paraffin produced; this excessive consumption of the isobutane is usually undesirable in commercial alkylation processes.

Direct evidence of this hydrogen transfer reaction in the presence of sulfuric acid was obtained in an investigation (Marschner and Carmody, 24) of the alkylation of isobutane with isoamylenes (as *t*-amyl alcohol) and of

isopentane with *n*-butylene (as *s*-butyl alcohol) or with isobutylene (as *t*-butyl alcohol or *t*-butyl chloride). In each case, isoparaffin was formed in amount equivalent to a large proportion of the olefin: isopentane was isolated in 40 to 50% of the theoretical yield based on the *t*-amyl alcohol, and isobutane in 70–110% yield based on the butyl derivative used. At the same time, much more than 1 mole of charged isoparaffin was consumed per mole of olefin derivative: about 1.8 moles of isobutane and about 2.2 to 2.7 moles of isopentane, respectively, reacted chiefly to yield octanes and decanes, part of which underwent destructive alkylation. The products of direct alkylation, nonanes, were formed in varying amount, depending on the reactants, the highest yield being obtained when *s*-butyl alcohol was used.

When isobutane was alkylated with 1- or 2-butene in the presence of aluminum chloride monomethanolate, very little or no *n*-butane was formed despite the fact that appreciable amounts of 2,2,4-trimethylpentane were produced (Schmerling, 14d). Similarly, no *n*-butane or *n*-pentane, respectively, was obtained by the alkylation of isobutane with 2-butene and with 2-pentene in the presence of sulfuric acid although trimethylpentanes were formed in both cases (McAllister *et al.*, 12; cf. Marschner and Carmody, 24). This apparent discrepancy in the alkylation mechanism may be explained readily. The *n*-alkylene is converted not into *n*-alkane, but into isoalkane. The resulting isobutane cannot, of course, be differentiated from that charged; the resulting isopentane, on the other hand, can be and was actually found in substantial yield. In other words, the proton transfer reaction is accompanied by rearrangement of the carbon skeleton of the carbonium ion.

Not only the isoparaffin but also the unsaturated hydrocarbon tied up in the catalyst complex serves as a hydrogen donor in the transfer reaction. The latter thus becomes more highly unsaturated.

3. Polymerization

Polymerization of the olefin is competitive with alkylation of the isoparaffin. It occurs under conditions which are unfavorable for rapid alkylation: low ratio of isoparaffin to olefin, spent catalyst, low catalyst to hydrocarbon ratio, too low temperature, and others.

Polymerization of the olefin probably proceeds via the reaction analogous to step 2. The olefinic polymerization product may be isolated as such or it may undergo hydrogen transfer with the isoparaffin with the resultant saturation of the double bond. Also, hydrogen disproportionation between two molecules of the polymer may occur, yielding one molecule of paraffinic product and one of the highly unsaturated material found in the catalyst complex (cf. Bartlett, Condon, and Schneider, 15, p. 1536).

4. Formation of Catalyst Complex

As has already been indicated hydrogen transfer reactions involving olefinic hydrocarbons lead to the formation of highly unsaturated compounds. These form addition complexes ("lower layer" or "sludge") with the catalyst. In this way, crystalline aluminum chloride is converted to a red-brown liquid. Similar red to brown viscous products are obtained when sulfuric acid or hydrogen fluoride is employed.

5. Formation of Esters

Alkyl esters are formed by addition of the hydrogen halide promoter used with aluminum halide or of hydrogen fluoride or sulfuric acid catalyst to the olefin. Their formation is also inherent in the reaction of the second step of the chain mechanism. If conditions are not favorable for the reaction of these esters with the isoparaffin (by the reaction of step 1 or step 3), the esters are obtained as impurities in the alkylate. In general, they are produced under the same conditions which led to polymerization rather than alkylation. Usually very little ester is present in the alkylation product.

IV. CATALYSTS

1. Aluminum Chloride

a. With Olefins. Although aluminum chloride was the first known catalyst for the alkylation of isoalkanes and has been intensively investigated, it has found less commercial application than the acid catalysts, sulfuric acid, and hydrogen fluoride. This is due primarily to the ease with which side reactions, particularly cracking, occur in its presence and to its relatively short life; special techniques must be employed in order to utilize it efficiently. On the other hand, in contrast with the acid catalysts, aluminum chloride readily catalyzes the alkylation of isoparaffins with ethylene in excellent yields and consequently has been used for the production of 2,3-dimethylbutane by the reaction of isobutane with ethylene.

Alkylation with ethylene proceeds best at temperatures above room temperature and under superatmospheric pressure. Ethylation of isobutane in batch operation at 25–35° in the presence of aluminum chloride and hydrogen chloride resulted in a product that was 45% hexanes. The hexane fraction was shown to consist of 70–90% 2,3-dimethylbutane, 10–25% 2-methylpentane, and less than 3% 2,2-dimethylbutane (Grosse and Ipatieff, 25). The catalyst was converted into the typical red-brown liquid lower layer complex.

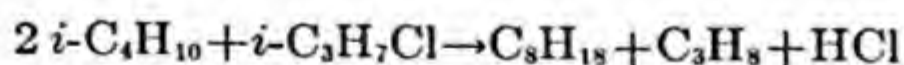
Alkylation of *n*-hexane with ethylene takes place under similar conditions (Ipatieff *et al.*, 26). It seems probable that isomerization to isohexane precedes the alkylation.

Large scale ethylation of isobutane involves the use of liquid aluminum chloride catalysts since these are more readily adaptable to continuous operation (Section IV, 2).

When aluminum chloride is used at room temperature as catalyst for alkylation with olefins of higher molecular weight than ethylene, the reaction is accompanied by so much side reaction that the primary products no longer predominate. Formation of by-products may be greatly minimized by carrying out the reaction at a sufficiently low temperature, for example, -30 to -35° (Pines, Grosse, and Ipatieff, 27). Continuous alkylation of isobutane with propene at -30° and atmospheric pressure in the presence of unmodified aluminum chloride plus hydrogen chloride promoter yielded a liquid product that was 42% heptanes (chiefly 2,3-dimethylpentane and some 2,4-dimethylpentane) and 20% decanes; 90% of the liquid boiled below 220° . Alkylation of isobutane with *n*-butylene (33% 1-butene, 67% 2-butene) under similar conditions (-35°) produced a liquid product consisting of more than 60% octanes and 12% dodecanes. Analysis by means of the Raman spectra indicated that the octanes included 2,5-dimethylhexane and 2,2,3-, 2,2,4-, and 2,3,4-trimethylpentane.

Batch alkylation of isobutane with 1-butene and with 2-butene at 30° resulted in deep-seated decomposition reactions, octanes comprising only 21–24% of the liquid products (Schmerling, 14d). Dimethylhexanes predominated in the 1-butene product (6.4% trimethylpentanes, 11.5% dimethylhexanes, and 3.5% methylheptanes). Trimethylpentanes were the principal octanes present in the 2-butene alkylate (14.5% trimethylpentanes, 5.8% dimethylhexanes, and 2.6% methylheptanes). The octane numbers of the 125° endpoint gasolines from the 1-butene and the 2-butene alkylations were 74.5 and 83.5, respectively.

b. With Alkyl Chlorides. Isoparaffins (unlike aromatic hydrocarbons) undergo little alkylation when treated with alkyl chlorides in the presence of aluminum chloride; instead, intermolecular hydrogenation occurs, the alkyl halide is reduced to the corresponding paraffin and hydrogen chloride, the hydrogen being furnished by the original isoparaffin which is thereby converted either to the paraffinic "self-condensation" product or to the unsaturated hydrocarbon combined with the aluminum chloride in the lower layer. The over-all reaction is similar to that of hydrogen transfer with olefins (Section III, 2).



The reduction is of course inherent in the hydrogen-chlorine exchange reaction which is the first step of the chain alkylation mechanism (Schmerling, 14).

The reaction of isobutane with isopropyl chloride in the presence of

aluminum chloride at 40 and 70° resulted in the formation of 60 and 90%, respectively, of the propane available by the reduction of the alkyl chloride (Schmerling, 28). The isobutane was converted mainly to octanes (and products of their destructive alkylation) and to catalyst complex. No reaction at all occurred when isobutane was heated at 70° with aluminum chloride and hydrogen chloride.

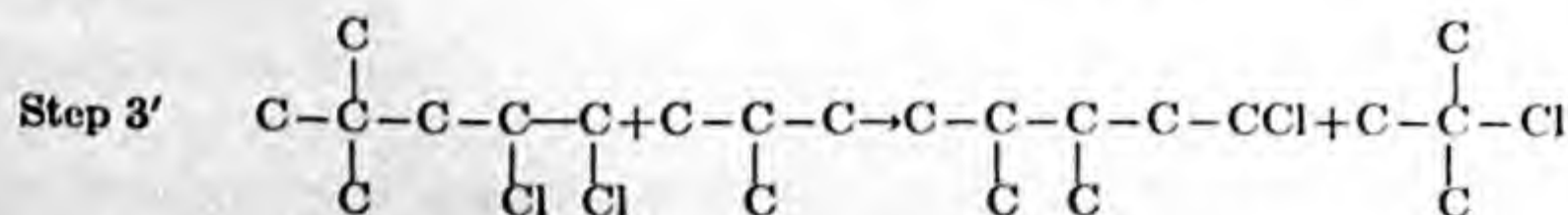
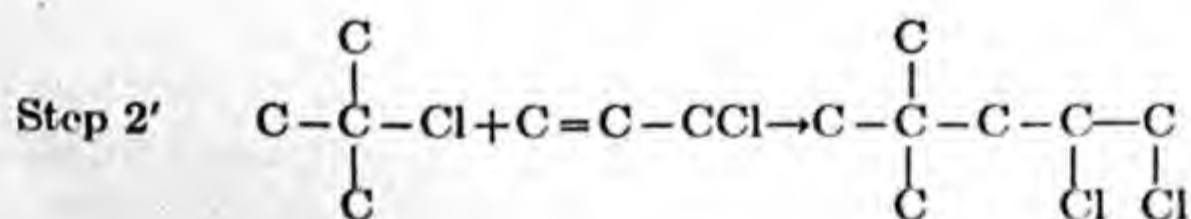
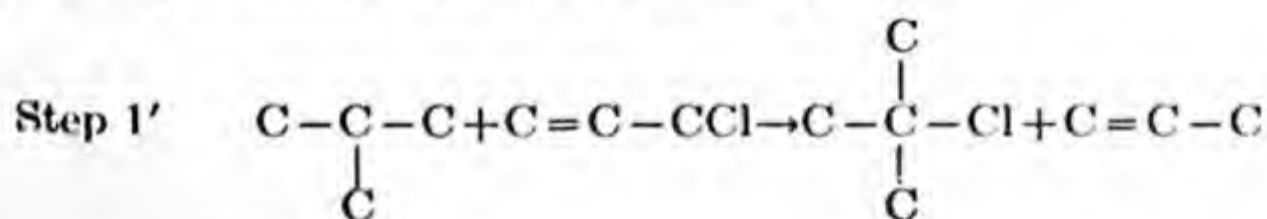
In an analogous manner, isopropyl chloride was converted to propane in 90% yield when it was heated at 40° with isopentane and aluminum chloride. Heating the isopentane with aluminum chloride and hydrogen chloride caused it to undergo autodestructive alkylation, yielding higher-boiling isoparaaffins and isobutane but no propane; less catalyst complex was formed than when isopropyl chloride was used.

It has been claimed that isobutane is alkylated by methyl and ethyl bromide when aluminum bromide is used as catalyst. This point is discussed in Section IV, 6.

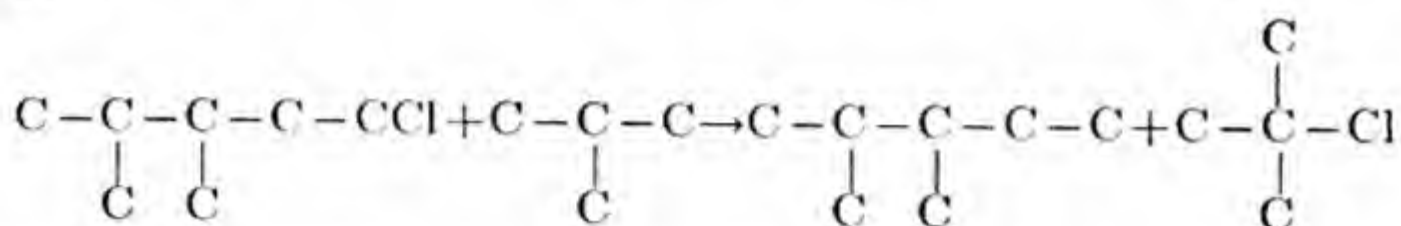
c. With Chloroolefins. Isobutane is chloroalkylated when it is contacted with allyl chloride in the presence of aluminum chloride at temperatures below about -10° (Schmerling, 14b). The major product, 1-chloro-3,4-dimethylpentane, is obtained in 35-40% yield at -10°; 1,2-dichloro-4,4-dimethylpentane is produced in 13-15% yield. On the other hand, what amounts to alkylation of the isobutane takes place when the reaction is carried out at higher temperatures, the product consisting essentially of paraffinic hydrocarbons because of interaction of the chloroheptanes with the isobutane. At 0-5°, for example, liquid paraffins were formed to the extent of 320% by weight of the propene available from the allyl chloride; this represents the reaction of 1.6 moles isobutane per mole allyl chloride.

The following mechanism, analogous to that suggested for alkylation with olefins, explains the experimental observations.

At temperatures below about -10°:



The *t*-butyl chloride formed in step 3' reacts with allyl chloride as in step 2', thus starting a new cycle. As previously mentioned, the reaction of the first step occurs only as an initiating step; the small amount of propene reacts either with isobutane (via *t*-butyl chloride) to yield heptane or with the catalyst to form lower layer complex. At temperatures above about -10° :



The *t*-butyl chloride may react with the catalyst to form lower layer or may be converted into octene or octyl chloride which is then converted to octanes.

The reaction of isobutane with vinyl chloride in the presence of aluminum chloride yielded liquid isoparaffins and 1,1-dichloro-3,3-dimethylbutane (40% yield at -10° and 20% yield at 25°). *t*-Butyl was isolated in about 10% yield. The formation of the dichlorohexane instead of monochlorohexane may be explained as being due to the relative unreactivity of the primary chlorine atoms; only a very small amount of the dichloride is reduced to monochloride by the reaction similar to step 3'. In the case of the allyl chloride reaction, the dichloroheptane contains a secondary chlorine atom and reacts readily with isobutane, yielding monochloroheptane and *t*-butyl chloride. Under conditions which are such as bring about the reduction of a chlorine atom of the dichlorohexane, both chlorine atoms are replaced, and the product consists of isoparaffins and only a very small amount of monochlorohexane.

Similarly, the condensation of isobutane with 1,2-dichloroethylene yields 1,1,2-trichloro-3,3-dimethylbutane as principal chlorine-containing product (Schmerling, 29). This trichloride is obtained in 35% yield by the reaction of isobutane with the *cis* isomer of the dichloroethylene at room temperature and in less than 5% yield by reaction with the *trans* isomer under the same conditions.

2. Aluminum Chloride Sludges

Because 2,3-dimethylbutane is a very desirable component of aviation gasoline and because aluminum chloride is a particularly suitable catalyst for the production of this hexane by the ethylation of isobutane, much work has been done to develop processes for carrying out the reaction on a commercial scale in continuous flow operation. Excellent results have been obtained with liquid aluminum chloride sludges consisting of aluminum chloride dissolved or dispersed in complexes of aluminum chloride with highly unsaturated hydrocarbons. These sludges are insoluble in the

alkylate, settle rapidly and may be separated from it very readily and recycled. They may be prepared by a number of methods. They may be formed *in situ* by the alkylation reaction or be produced by the action of aluminum chloride on olefins or such substances as isooctane, kerosene, or similar hydrocarbon fractions. Two groups of investigators (Alden *et al.*, 30 and Thompson and Chenicek, 31) have discussed the results obtained with the liquid sludge formed during the alkylation of isobutane with ethylene. Another group (Holloway and Bonnell, 32) has described the use of the sludge prepared by the action of aluminum chloride on the high-boiling residue (b.p. 161–195°+) from the distillation of sulfuric acid alkylate (formed by the alkylation of isobutane with propene and butenes).

An important advantage of the sludge catalysts is that they can be maintained at a constant uniform level of activity by the addition of small amounts of fresh catalyst. When preformed sludge, such as that formed by the action of aluminum chloride on alkylate bottoms is used, the makeup catalyst may be pumped into the reaction mixture, an equivalent amount of spent catalyst being removed at the same time (Holloway and Bonnell, 32). When the sludge is formed *in situ*, fresh aluminum chloride may be added as such at spaced time intervals (Alden *et al.*, 30) or continuously as a solution in the isoparaffin. The latter is conveniently accomplished by passing all or a portion of the isobutane through a heated zone (a "saturator") containing granular aluminum chloride (Thompson and Chenicek, 31). The bulk supply of the catalyst is not contaminated inasmuch as isobutane does not react with aluminum chloride at the temperatures used (about 60°) in the absence of a promoter. This method is flexible and exact since the amount added can be controlled by regulating the temperature or the rate of flow of the isobutane. It has the advantage that the separate sludge manufacture step is eliminated and that there is no need for relatively complicated fresh sludge pumping means. Furthermore, the yield of alkylate per unit weight of aluminum chloride is increased because no catalyst activity is wasted merely to form the sludge.

Less side reaction occurs with the sludge catalysts than with unmodified aluminum chloride. Excellent yields of alkylate containing as much as 80% by volume of hexane were obtained in the continuous alkylation of isobutane with ethylene (in about 5 to 1 ratio) at 60° in the presence of sludge plus fresh aluminum chloride added in isobutane solution using hydrogen chloride as promoter (Thompson and Chenicek, 31). Similar yields of product containing 70–75% of hexanes were obtained at 56–59° with preformed sludge and in the absence of added hydrogen chloride (Holloway and Bonnell, 32). In the former experiments, the reactor was a turbomixer; in the latter, a jet reactor was used.

As has just been indicated, no hydrogen chloride was added in the

experiments made with the preformed sludge. Holloway and Bonnell state that since it was found possible to secure alkylation without the addition of hydrogen chloride and since this is advantageous, no data were accumulated on the effect of varying amounts of the promoter. They point out that the catalyst was prepared without the addition of promoter and that any free hydrogen chloride formed in its preparation was worked out of the sludge during the cooling and stirring procedure. Furthermore, free hydrogen chloride was not found in the catalyst upon analysis. They conclude, "Thus it does not appear that appreciable concentrations of free hydrogen chloride could have been present in these runs, although it cannot reasonably be denied that traces such as would be required in a recently proposed alkylation mechanism (Schmerling, 14c) may have existed."

Holloway and Bonnell are probably correct in their assumption that only traces of hydrogen chloride (or other chlorine-containing compound which can act as chain initiator) need be present in order that alkylation can occur. It is furthermore reasonable to assume that an additional trace amount was continually added with the makeup sludge. On the other hand, experiments in which sludge formed *in situ* was used have shown that the presence of substantial quantities of promoter has a marked effect on the catalyst life and hence on the yield of alkylate per unit weight of aluminum chloride (Thompson and Chenicek, 31). It was found that when no promoter was used, the yield of alkylate, and the percentage of hexanes in the alkylate, decreased rapidly as the run progressed. Satisfactory results were obtained with from 0.5 to 5.2 mole % hydrogen chloride (based on the total charge). The composition of the products was excellent in all cases (the alkylate containing 79–86% of hexanes) but the yield of alkylate decreased with increase in hydrogen chloride concentration from 2.1 to 5.2%, which suggested that ethylene was removed from the reaction by combining with the hydrogen chloride to form ethyl chloride. This was confirmed by analyzing the exit gas (ethyl chloride forms an azeotrope with *n*-butane) and it led to the use of ethyl chloride instead of hydrogen chloride as promoter. It was found that alkylate yields approaching the theoretical were obtained at 60° in the presence of 1.8 mole % ethyl chloride; 80% by volume of the alkylate was hexane and 98% boiled below 150°. There was little net consumption of ethyl chloride. Traces of ethane were formed which indicates that the function of the ethyl chloride probably is to initiate the chain reaction of alkylation. The fact that ethyl chloride rather than hydrogen chloride is found in the existing gas may explain why Holloway and Bonnell found no hydrogen chloride in the sludge.

Further evidence that addition of hydrogen chloride promoter has a beneficial effect may be seen in the fact that catalyst life is greatly increased.

A life test lasting 54 days was carried out (Thompson and Chenicek, 31); during this time 65 g. of fresh aluminum chloride was introduced from the saturator and 47.1 l. of total alkylate was produced. This is equivalent to a yield of 85 gallons alkylate per pound aluminum chloride consumed. On the other hand, it was found (Holloway and Bonnell, 32) that the catalyst life obtained with sludge formed *in situ* (but using a jet reactor instead of a turbomixer) and in the absence of added promoter was 26 gallons alkylate per pound aluminum chloride. When the preformed sludge was used (again without added promoter), it was not found possible to obtain a catalyst life greater than 17.2 gallons alkylate per pound aluminum chloride.

The alkylate obtained in the life test reported by Thompson and Chenicek contained 80.7% by volume hexanes and about 12% octanes. The hexanes consisted of 92% 2,3-dimethylbutane, 1-2% 2,2-dimethylbutane, and 7% of 2-methylpentane as shown by infrared analysis. Thus, more than 72% of the total alkylate was 2,3-dimethylbutane. The octane fraction was essentially 2,2,4-trimethylpentane.

The effect of the composition of the aluminum chloride hydrocarbon complex on the yield and quality of alkylate was investigated by recycling the sludge at 60° without adding any fresh aluminum chloride; hydrogen chloride was used as promoter (Thompson and Chenicek, 31). It was found that the aluminum chloride content of the sludge slowly decreased because of the gradual accumulation of hydrocarbons in the complex. A catalyst of excessively high aluminum chloride content (90-92%) gave a fair yield of alkylate (253-276% by weight of the ethylene charged) but its hexane content was only 49-57% by volume. As the run progressed and the aluminum chloride content dropped to 82-84%, the alkylate yield was 300-316% and the hexane content was quite constant at 73-74%. The optimum aluminum chloride content appeared to be 63-84%.

That the increase in hydrocarbon content is not due to replacement of either chlorine or aluminum seems to be proved by the observation that the chlorine to aluminum atomic ratio was relatively constant at 2.2-2.5 throughout the course of a run. (The chlorine values were based on ionizable halogen. The fact that the ratio was not 3.0 is significant. It seems to indicate that chlorination of hydrocarbon material occurred with the resultant formation of hydrogen chloride or alkyl chloride. Such chlorine-containing material, much of which might be tied up in the catalyst complex, could react in the chain-initiating step of the alkylation, thus making addition of promoter unnecessary during the earlier part of the sludge's use.)

The effect of changes in a number of other variables (temperature, pressure, contact time, isobutane to ethylene ratio, and diluents) on the

yield and quality of the alkylate has also been investigated. Discussion of the results as well as of those obtained in commercial production of 2,3-dimethylbutane is, however, beyond the scope of this paper.

3. Aluminum Chloride Monomethanolate

The addition complex of equimolar amounts of aluminum chloride and methanol is a crystalline compound which is stable at temperatures below 70°; at higher temperatures it decomposes, forming hydrogen chloride and methoxyaluminum dichloride, further heating of which yields methyl chloride and oxyaluminum chloride (Norris and Sturgis, 33). It very readily catalyzes the alkylation of benzene, in which it is soluble, and of isobutane, in which it is not (Schmerling, 14d). On the other hand, the product of the reaction of aluminum chloride with two molecular proportions of methanol (i.e., $\text{AlCl}_3 \cdot 2 \text{CH}_3\text{OH}$) is not an alkylation catalyst.

The activity of aluminum chloride monomethanolate promoted by hydrogen chloride is such that alkylation of isobutane with propene or butene takes place at room temperature or higher with comparatively little side reaction, thus making possible the isolation of primary reaction products. Heptane comprised 52% of the liquid obtained by the reaction of isobutane with propene at 62°. The heptane consisted of nearly equal amounts of 2,3- and 2,4-dimethylpentane. With 1-butene as the alkylating agent at 55°, the alkylate contained 60% dimethylhexanes (35% 2,4- and 2,5-, 17% 2,3- and 8% 3,4-dimethylhexane) and 9.5% trimethylpentanes (6.5% 2,2,4- and 3% 2,3,4-trimethylpentane). With 2-butene at 28°, the products included 65% trimethylpentanes (28% 2,2,4-, 22.5% 2,3,4-, 14% 2,3,3-, and 0.5% 2,2,3-trimethylpentane) and 4% dimethylhexanes (3.5% 2,4- and 2,5- and 0.5% 2,3-dimethylhexane). With 2-butene at a higher temperature, namely 64°, the trimethylpentanes comprised 44% and the dimethylhexanes 7%, of the liquid product. The octane numbers of the 125° end-point gasoline obtained with 1-butene and with 2-butene were 76 and 92-94, respectively.

Although the alkylation with 1-butene proceeded smoothly at 55°, relatively little alkylation occurred at 28°, a temperature which gave very satisfactory results with 2-butene. That the ease of alkylation with 1-butene at the higher temperature was not due to intermediate isomerization to 2-butene is evident from the composition of the products.

It is worthwhile to compare these results with those obtained with pure aluminum chloride as catalyst at 30° (Section IV, 1a).

The significance of the fact that the major product of the alkylation with 1-butene was dimethylhexanes while that with 2-butene was trimethylpentanes has been discussed in the section on the mechanism of the reaction.

4. Aluminum Chloride-Nitroalkane Solutions

Aluminum chloride dissolves in as little as its own weight of the readily available nitroparaffins, nitromethane, nitroethane, and the two nitropropanes. The resulting solutions, particularly those employing nitromethane, are catalysts for the alkylation of isobutane, hydrogen chloride serving as a promoter (Schmerling, 28). On the other hand, solutions of aluminum chloride in molecular excess of ethers, ketones, and alcohols are catalytically inactive, at least for the alkylation of hydrocarbons.

The active component of the nitroparaffin solutions of aluminum chloride has been shown to be not the metal chloride per se but rather the addition compound, $\text{AlCl}_3 \cdot \text{RNO}_2$. In this connection it is significant to contrast the nitroparaffin solutions with the ether, ketone, and alcohol solutions. All four types of compounds form monomolecular addition complexes (usually crystalline compounds of low melting point) which are catalytically active (Schmerling, 34). For example, aluminum chloride monomethanolate, as was shown above, catalyzes the alkylation of isoparaffins. Solutions of the aluminum chloride monomethanolate in excess methanol are, however, catalytically inert; indeed, even the solid product of the reaction of aluminum chloride with two molecular proportions of methanol (i.e., $\text{AlCl}_3 \cdot 2 \text{CH}_3\text{OH}$) is not an alkylation catalyst. Similarly, aluminum chloride monoetherates and monoketonates lose their catalytic activity when dissolved in ethers and ketones, respectively. In direct contrast with these, the aluminum chloride nitroparaffin complexes retain their activity even with a large excess of the nitroparaffin solvent.

a. With Olefins. Alkylation of isoparaffins with olefins took place in best yield when nitromethane was used as solvent for the aluminum chloride. The nitroethane and 1-nitropropane solutions gave fair to good yields of alkylated product while rather poor yields were obtained with the 2-nitropropane solutions.

Higher reaction temperatures are required with these catalysts than with unmodified aluminum chloride. Alkylation of isobutane with propene at 35° in the presence of a nitromethane solution of aluminum chloride promoted by hydrogen chloride gave a yield of liquid product amounting to only 110% by weight of the propene charge; the yields of heptanes and of octanes were, respectively, 9 and 6% by weight of the propene. Carrying out the reaction at a higher temperature, 70° , resulted in a 200% yield of alkylate, a 105% yield of heptanes, and a 29% yield of octanes. The heptanes, which were thus produced in 44% of the theoretical amount, consisted chiefly of 2,3- and 2,4-dimethylpentane. The octane was formed by the hydrogen transfer side reaction; propane was found in approximately equimolar quantity.

The catalyst solutions were not soluble in the paraffinic product. They

underwent little change in weight during the reaction and were recovered as brown mobile liquids.

b. With Alkyl Chlorides. It was shown in Section IV, 1b that isopropyl chloride is converted to propane in 60–90% yield when it is treated with isobutane or isopentane in the presence of aluminum chloride. It is, therefore, of interest to note that the use of nitromethane solutions of aluminum chloride permits the alkylation of the isoparaffins with isopropyl chloride. Less than 30% of the isopropyl chloride was reduced to propane when it was heated with isobutane at 70° in the presence of the catalyst solution. The liquid product (100% by weight of the available propene) consisted of a mixture of paraffins, heptanes, and octanes being formed in largest amount (35 and 20% respectively). The yield of liquid product was higher than that (70–75%) obtained in the presence of unmodified aluminum chloride.

The reaction of isopentane with isopropyl chloride at 70° in the presence of the nitromethane solution of aluminum chloride yielded octane (42% by weight of the available propene) as the major product. Propane was formed in only 15% yield. Little or no reaction occurred when either isopentane plus hydrogen chloride or isopropyl chloride was heated at 60–70° with the nitromethane solution of aluminum chloride.

5. Aluminum Chloride-Alkali Metal Chloride Double Salts

Aluminum chloride forms double salts of relatively low melting point (e.g., 140–300°) with a large number of metallic chlorides. The use of such addition compounds with equimolar quantities of sodium chloride, lithium chloride, ammonium chloride, or potassium chloride as catalysts for the alkylation of isobutane with ethylene, propene, or isobutylene has been described (Blunck and Carmody, 35). Temperatures of at least 150° at pressures of about 1000 p.s.i. were found to be necessary for alkylation when a mixture of isobutane and the olefin was passed, at a space velocity of 1–5 cc./cc. catalyst/hour, over the double salt deposited on pumice. The activity of the double salts decreased in the order mentioned, the potassium chloride compound being quite inactive but yielding some polymerization product at 316°.

The product obtained with ethylene in the presence of the sodium chloroaluminate catalyst at about 150–170° was completely paraffinic but the yield was low: 75–90% weight of the ethylene charge. Higher yields were obtained with propane and isobutylene, but the product contained substantial quantities of olefins formed by the competing polymerization reaction.

Catalyst life was very poor. However, it should be noted that hydro-

gen chloride promoter was not used in this study. Further investigation is required before final conclusions as to the catalytic behavior of these double salts can be made.

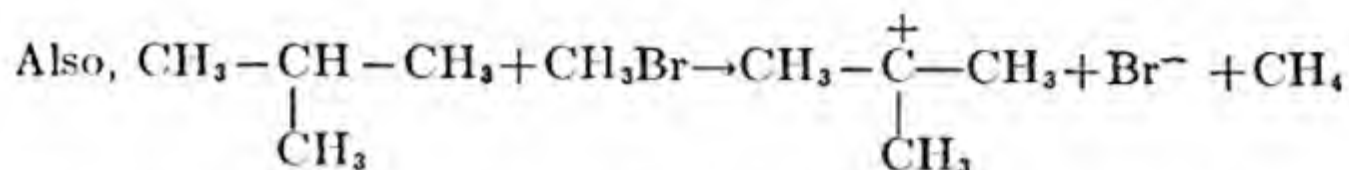
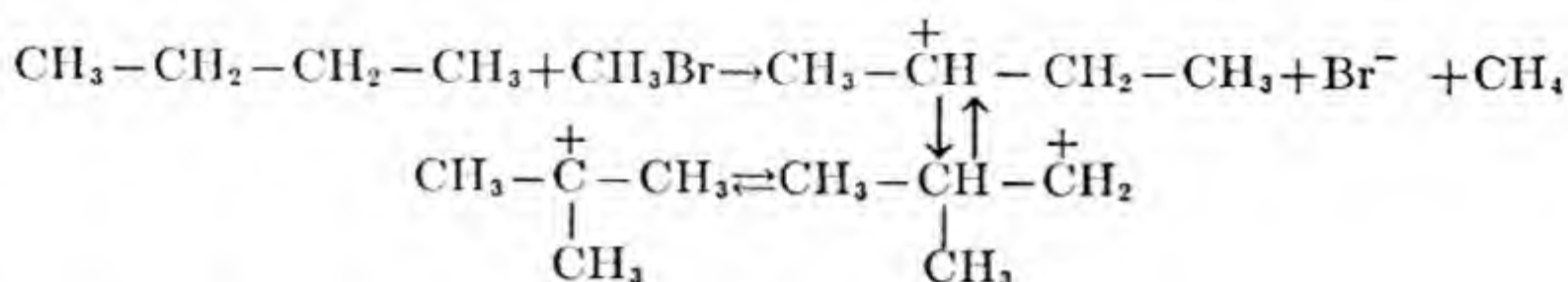
6. Aluminum Bromide

No detailed discussion of the use of aluminum bromide as catalyst for the alkylation of paraffins with olefins has been published. Alkylation presumably takes place in much the same manner as with aluminum chloride, the chief difference being that the catalyst is soluble in the paraffin.

Alkylation of *n*-butane and isobutane with methyl or ethyl bromide in the presence of aluminum bromide has been claimed (Heldman, 36). It was found, for example, that the action of aluminum bromide (0.00158 mole as Al_2Br_6) on a solution of 0.0392 mole methyl bromide in 0.0750 mole *n*-butane at 25° for 120 hours yielded 0.0052 mole isopentane (13% of the theoretical based on the methyl bromide); isobutane was also formed. In a similar experiment carried out at 78° for 65 hours, the yield of isopentane was 33%. The reaction of isobutane (0.0520 mole) with methyl bromide (0.0392 mole) in the presence of aluminum bromide (0.00142 mole Al_2Br_6) at 25° for 283 hours yielded low boiling material (0.0009 mole), *n*-butane (0.0062 mole), unreacted isobutane (0.0410, 79% of that charged), isopentane (0.0034 mole, 9% of the theory) and higher boiling material (0.0024 mole).

Analogous results were obtained with ethyl bromide. The action of aluminum bromide on a solution of 0.0262 mole ethyl bromide in 0.0500 mole *n*-butane at 25° for 42 hours yielded 0.0150 mole material boiling higher than *n*-butane. With isobutane (0.0741 mole), ethyl bromide (0.0642 mole), and aluminum bromide (0.00310 mole Al_2Br_6) at 50° for 48 hours, there was obtained a trace of methane, 0.0140 mole ethane (22% of the theoretical based on the ethyl bromide), 0.0080 mole propane, 0.0082 mole *n*-butane, 0.0185 mole (25% of that charged) isobutane, 0.0130 mole isopentane (20 mole % of the ethyl bromide charge), and 0.0095 mole hexane and higher.

The present authors question whether these results prove that the alkyl bromides (particularly methyl bromide) actually underwent condensation with the butanes. In most of the experiments no data are given to show how much methane or ethane was formed. For none of the experiments is the amount of unreacted methyl or ethyl bromide recorded. It is quite possible that hydrogen-halogen exchange occurred and that the isopentane and the higher-boiling paraffins were formed entirely from the butane.



The *t*-butyl carbonium ion (or *t*-butyl bromide) may undergo disproportionation reactions of the type outlined in the sections on destructive alkylation and hydrogen transfer to yield isopentane and higher-boiling paraffins.

Further experiments are, therefore, required before it can be stated definitely that the methyl group of the methyl bromide is present in the final alkylate. The desired information might be obtained by carrying out larger scale tests with more accurate analysis of all of the products. It would almost certainly be obtained from experiments employing methyl bromide containing radioactive carbon. If methylation of the butane predominates, the isopentane will be radioactive; if reduction of the type shown above occurs, the radioactive carbon will be found in the methane.

7. Boron Fluoride

Boron fluoride, promoted by a minor amount of hydrogen fluoride or water, seems to catalyze the alkylation of isoparaffins with ethylene at lower temperatures than does aluminum chloride (Grosse and Ipatieff, 25). The reaction of isobutane with ethylene to -30 to -40° and 6 atmospheres pressure yielded a liquid product, 20% of which was hexanes, to the extent of 180% by weight of the ethylene charged. At $0-5^\circ$ and 10 atmospheres pressure, a 224% yield of alkylate, 45% of which was hexanes, was obtained. Like the aluminum chloride product formed at $25-35^\circ$, the hexanes consisted of 70-90% of 2,3-dimethylbutane, 10-25% of 2-methylpentane, and 3% of 2,2-dimethylbutane.

Alkylation of isobutane with isobutylene at 25° in the presence of boron fluoride promoted by water yielded an alkylate which contained 32% octanes and 15% dodecanes (Ipatieff and Grosse, 37).

8. Zirconium Chloride

The action of zirconium chloride in the alkylation of isoparaffins with olefins and in other hydrocarbon reactions is very similar to that of aluminum chloride, the principal difference being that it requires higher temperatures. Comparatively little information concerning its use has, however, been published.

Alkylation of isobutane with ethylene in the presence of zirconium chloride took place at 100° under 15 atmospheres pressure (Ipatieff, 1, p. 682). The product was completely paraffinic and consisted chiefly of hexanes, octanes, and decanes. The catalyst was converted to a dark, pasty mass which was still catalytically active as was shown by its re-use in a second experiment with isobutane and ethylene.

The alkylation of isobutane with *n*-butylene was subsequently carried out by gradually adding an equimolar mixture of the paraffin and the olefin to a stirred mixture of zirconium chloride and a minor amount of isobutane in the presence of hydrogen chloride (Ipatieff, Friedman, and Schmerling, 38). At 23° and 6 atmospheres pressure, there was formed a liquid product (bromine number, 18) which contained 81% material boiling below 225°, of which about 46% was octanes and 18% was dodecanes. The liquid product obtained at 50° and 7 atmospheres had a lower bromine number, 3; it contained 79% of material boiling below 225°, of which about 58% was octanes and 19% was dodecanes. The octanes consisted principally of trimethylpentanes. The A.S.T.M. octane number of the material boiling at 95–116° (85% of the total octane fraction) was 91.

9. Sulfuric Acid

a. With Olefins. Concentrated sulfuric acid is an excellent catalyst for the alkylation of isoparaffins with propene and higher molecular weight olefins; it does not readily catalyze alkylation with ethylene, presumably because stable ethyl hydrogen sulfate is formed. Best results are obtained with 96–98% acid. Stronger acid is required for alkylation with propene than with the higher-boiling olefins; acid strengths as high as 101.7% have been used with propene. The acid forms complexes (sludges) with highly unsaturated hydrocarbons during the alkylation and gradually loses its activity as an alkylation catalyst. Water formed by side reactions during the alkylation or introduced with the hydrocarbons further serves to dilute and weaken the catalyst. In the continuous alkylation of isobutane with propene and the butylenes the acid concentration can drop to 90% without markedly affecting the product; with amylenes, 85% acid is satisfactory. If the acid concentration drops below these strengths, polymerization of the olefin becomes the chief reaction. In commercial operation the concentration of the acid is maintained at the desired level by withdrawing a portion of the used acid and adding makeup catalyst of 96–100% strength.

Suitable alkylation temperatures lie in the range 0–30°. The optimal temperature depends on the olefin and the catalyst strength. In general, higher temperatures can be employed with propene than with the butylenes and higher-boiling olefins. The lower the temperature, the higher is the strength of the acid which is required. Thus, alkylation of isobutane with

propene in the presence of 98% sulfuric acid proceeded smoothly at 30°, yielding 213% alkylate by weight of the propene; 90% of the alkylate was aviation gasoline boiling below 150° (McAllister *et al.*, 12). Little or no alkylation occurred in the presence of 97% sulfuric acid at 20°; instead isopropyl hydrogen sulfate and polymers and hydropolymers were obtained (Birch *et al.*, 21b). Satisfactory results were obtained at this temperature by employing a stronger acid, 101.7%; 215% by weight of alkylate, over 90% of which boiled below 150° was obtained. The octane numbers of the aviation gasoline fraction obtained in the two experiments cited were virtually the same, 88.5 and 89.1, respectively.

When the butylenes or amylenes are used as alkylating agents, temperatures above 20° result in poor yields of product based on the weight of both the olefin and the catalyst because oxidation of olefin occurs with the accompanying formation of sulfur dioxide. At 20° with 97% sulfuric acid, alkylation of isobutane with 1-butene and 2-butene, respectively, resulted in 159 and 164% yields of alkylate, containing 88 and 90% 185° end-point gasoline of 89.1 and 90.2 octane number when a 1 to 1 ratio of isoparaffin to olefin was used (Birch *et al.*, 21a). With a 4 to 1 ratio, the respective alkylate yields were 183 and 199%; the 185° end-point gasolines (92 and 91%, respectively, of the alkylates) had octane numbers of 92.9 and 93.0. At 10° with 100% sulfuric acid, a 200% yield of alkylate, 93% of which boiled below 150° and had an octane number of 94, was obtained (McAllister *et al.*, 12) by the alkylation of isobutane with 2-butene (5 to 1 ratio). When isobutylene was the alkylating agent (7 to 1 ratio), use of 98% sulfuric acid at 20° yielded 180% of alkylate, only 81% of which boiled below 150° and had an octane number of 91.5 (McAllister *et al.*, 12).

In the commercial alkylation of isobutane with the butylenes, temperatures between 0 and 10° are employed because catalyst life is increased with a decrease in temperature. The strength of the makeup acid is 98–100%. Temperatures below 0° are not used because the emulsified mixture of catalyst and hydrocarbons becomes too stiff to flow readily.

Intimate contact of the catalyst and the hydrocarbon mixture is essential for high yields of alkylate and low acid consumption. Mole ratios of isoparaffin to olefin in the range 5 to 1–10 to 1 and volume ratios of acid to hydrocarbon of about 1 to 1 give the best results. Contact times of about 20–40 minutes are usually employed.

Typical yields of alkylate obtained in plants operated during World War II were in the order of 1–2 gallons per pound of catalyst in the alkylation of isobutane with butylenes and only about 0.5 gallon per pound for alkylation with propene or amylenes (Anonymous, 39). The octane numbers of the alkylates (175° end point) obtained with butylenes, propene, and amylenes were about 92–94, 88–89, and 89–90, respectively.

Alkylation of isopentane with 2-butene at 10° in the presence of 100% sulfuric acid resulted in a 264% yield of alkylate based on the olefin (McAllister *et al.*, 12). The theoretical yield for the simple alkylation reaction is 228%. Isobutane, hexanes (chiefly 2-methylpentane), nonanes, and decanes were formed. Destructive alkylation and hydrogen transfer occurred (Section III).

Neohexane did not react when contacted with 2-butene at 10° in the presence of 100% sulfuric acid (McAllister *et al.*, 12). Under similar conditions, alkylation of isohexane (a mixture of 2- and 3-methylpentane) yielded alkylate to the extent of 206% by weight of the 2-butene. It therefore appears that isoparaaffins that contain tertiary carbon atoms are more susceptible to alkylation.

The composition of a large number of alkylates, both those prepared in the laboratory using pure hydrocarbons and those obtained on a commercial scale using olefin mixtures, has been investigated. The principal products are for the most part similar to those obtained in the presence of the metal halide catalyst, the chief difference being in the relative amounts of the various isomers. Alkylation of isobutane with propene at 30° in the presence of 98% sulfuric acid yielded an alkylate that was 62–66% by weight 2,3-dimethylpentane and 8–12%, 2,4-dimethylpentane; propane and trimethylpentanes (11–19%) were also obtained (McAllister *et al.*, 12). A commercial isobutane-propene alkylate obtained at 21° was shown to contain about 36% by volume of 2,3- and 26% of 2,4-dimethylpentane as well as 15% of trimethylpentanes (Glasgow *et al.*, 40).

The product obtained by the alkylation of isobutane with 2-butene at 10° in the presence of 100% sulfuric acid contained 34–38% 2,2,4-trimethylpentane and 51–55% 2,3,4- and 2,3,3-trimethylpentane (McAllister *et al.*, 12). *n*-Butane was not obtained; the significance of this observation was discussed above (p. 42). Alkylation of isobutane with isobutylene at 20° in the presence of 98% acid yielded an alkylate which contained 24–28% by weight of 2,2,4-trimethylpentane and 30–34% of 2,3,4- and 2,3,3-trimethylpentane, as well as 7–9% of isopentane and 8–10% of 2,3-dimethylbutane formed by destructive alkylation (McAllister *et al.*, 12).

The significance of the fact that alkylation of isobutane with 1-butene yields a product which is very similar to that obtained with 2-butene has already been discussed (Section II).

Because of the importance of the alkylate prepared from isobutane and butylene in the aviation gasoline program during World War II, a number of commercial products were analyzed, with the view of determining the factors which would result in the maximum yields of fuels of high octane number (Glasgow *et al.*, 40; Field and Gould, 41). The A.S.T.M. octane numbers of three alkylates produced under decreasing throughput

ranged from 91.9 to 96.7, the best product being obtained by use of an extremely high ratio (33.5) of isobutane to butylene. The analytical results showed that all three alkylates contained essentially the same relative proportions of the four trimethylpentanes but the total trimethylpentane content of the alkylate varied from 56.1% by volume for the product of lowest octane number to 86.7% for that of highest octane number. Less dimethylhexane was present in the latter alkylate.

Evidence of a rather large extent of hydrogen transfer may be found in experiments with isobutane and olefins (particularly those containing tertiary carbon atoms?) of higher molecular weight than the butylenes (McAllister *et al.*, 12; cf. Marschner and Carmody, 24, discussed in Section III, 2). Thus, the alkylation of isobutane with 2-pentene yielded a product containing 6–8% of isopentane, 14–22% of trimethylpentanes, and 55–65% of nonanes; that obtained with 2-methyl-2-butene contained 18–20% of isopentane, 29–33% of trimethylpentanes, and only 15–20% of the expected nonanes. Similarly, alkylation of isobutane with the octene prepared by the dehydration of 2-ethyl-1-hexanol resulted in a product containing 35% of 3-methylheptane. Alkylation of isobutane with propylene trimers yielded nonane (45% of the alkylate) which corresponded closely to that obtained by hydrogenating the trimer; trimethylpentanes (33–40% of the alkylate) were formed in approximately the same molar amount as the nonanes. Hydrogen transfer was also the principal reaction that occurred when isobutane was contacted with diisoamylenes at 10° in the presence of 100% sulfuric acid. Decanes and trimethylpentanes comprised 16–20% and 40–50%, respectively, of the alkylate; isopentane (10–12%) was also produced, presumably by depolymerization of the diisoamylenes followed by hydrogen transfer. No nonanes (formed by depolyalkylation) or tetradecanes were obtained.

Depolyalkylation does occur when isobutylene polymers are used (McAllister *et al.*, 12). Thus the reaction of isobutane with butylene trimer at 10° produced an alkylate containing 60–65% trimethylpentane and 10–15% dodecanes which were presumably formed by hydrogen transfer; the relative yields of trimethylpentanes and dodecanes indicate that depolyalkylation occurred. A similar product was obtained by the reaction of isobutane with hot acid codimer of isobutylene and *n*-butylene (largely 2,2,4-, 2,2,3-, and 2,3,4-trimethylpentenes). These observations were confirmed in commercial alkylations. Alkylation with the dimer of 2-butene yielded an alkylate which had quite similar boiling point properties but a lower octane number (88 as compared to 93 for each of the other products). The presence of dimethylhexanes, formed by hydrogen transfer, is indicated.

b. With Alkyl Sulfates. The alkylation of isoparaffins with alkyl hydrogen sulfate or with dialkyl sulfate has received little study. Only one

experiment appears to have been described (Birch *et al.*, 21b). The reaction of isobutane with diisopropyl sulfate at -12° in the presence of commercial sulfuric acid resulted in a 65% yield (by weight of the propene "content" of the diisopropyl sulfate) of hydrocarbon with a boiling range of $88-244^{\circ}$. No reaction occurred when the sulfate and isobutane were contacted under similar conditions but in the absence of sulfuric acid. The use of higher reaction temperatures for the acid catalyzed reaction is indicated. Determination of the composition of the product would be of interest in connection with the alkylation mechanism.

c. With Alcohols. Alkylation of isoparaaffins with alcohols was carried out in an investigation (Marschner and Carmody, 24) of hydrogen transfer (cf. p. 41). The reaction of isobutane with *t*-amyl alcohol at 2° in the presence of 98.6% sulfuric acid yielded 248% liquid paraaffins (including isopentane formed by hydrogen transfer) by weight of the amylene available from the alcohol; the theoretical yield of alkylate is 183%. The product contained about 20% by weight isopentane, 46% octanes, and 9% nonanes. The nonanes represented 13% of the theoretical yield; the octanes and isopentane, 70 and 50% yields, respectively, assuming the interaction of two moles of isobutane with one of alcohol.

Similarly, alkylation of isopentane with *t*-butyl alcohol under the same conditions resulted in the formation of alkylate (boiling above pentane) to the extent of 305% by weight of the available isobutylene. The product contained about 21% by weight hexanes, 6% heptanes, 9% octanes, 27% nonanes, and 25% decanes. Nonanes were thus formed in 36% of the theoretical yield. Decanes and isobutane, respectively, were isolated in 30% and 111% of the yields obtainable if all of the *t*-butyl alcohol had undergone hydrogen transfer and none simple alkylation to form nonanes. Extensive destructive alkylation of the decanes apparently occurred.

Alkylation of isopentane with *s*-butyl alcohol at 24° resulted in 44% of the theoretical yield of nonanes and 18 and 72% yield decanes and isobutane, respectively, as well as substantial amounts of hexanes and octanes.

d. With Alkyl Chlorides. *t*-Butyl chloride has also been used as an alkylating agent for isoparaaffins in the presence of sulfuric acid (Marschner and Carmody, 24). The reaction of isopentane with *t*-butyl chloride at 13° in the presence of 98.6% sulfuric acid resulted in a 262% by weight yield (based on the isobutylene available from the chloride) of hexanes and higher-boiling paraaffins. Isobutane, nonanes, and decanes were formed, respectively, in 87, 27, and 28% of the theoretical yields.

10. Hydrogen Fluoride

a. With Olefins. Like sulfuric acid, hydrogen fluoride readily catalyzes the condensation of isoparaaffins with propene and higher molecular weight

olefins (Linn and Grosse, 19). Unlike sulfuric acid, it is very stable and is not readily oxidized or reduced. This chemical property, together with its low melting and boiling points, -83° and 19.4° , respectively, gives hydrogen fluoride a number of advantages as an alkylation catalyst. The reaction can be carried out over a wide range of temperatures and the catalyst may be recovered and re-used almost indefinitely. In commercial alkylation, for example, atmospheric or slightly superatmospheric temperatures are used, making refrigeration unnecessary; in the laboratory, temperatures as low as -25° or even lower may be employed. The spent catalyst can be regenerated merely by heating. Not only is the uncombined hydrogen fluoride thus distilled from the catalyst sludge, but the sludge itself is decomposed and the hydrogen fluoride which it contains is recovered. Similarly, substantially all of the fluorine content of the alkylate is recoverable as hydrogen fluoride by thermal or catalytic treatment. Catalyst consumption is, therefore, very low. Sixty to eighty-five gallons of alkylate per pound of hydrogen fluoride are obtained in commercial operation (Anonymous, 39).

Anhydrous hydrogen fluoride is the preferred catalyst because it does not corrode iron equipment under the alkylation conditions and because the presence of more than a small percentage of water has a detrimental effect on the yield of alkylate. Thus, hydrogen fluoride containing 10% by weight of water yielded isopropyl fluoride but practically no alkylate when employed as catalyst for the alkylation of isobutane with propene at 25° (Linn and Grosse, 19). Under the same conditions, use of a catalyst containing 1% of water resulted in a 214% yield of alkylate by weight of the propene. Somewhat more water can be tolerated with higher molecular weight olefins. The reaction of isobutane with *n*-butylenes at 25° in the presence of catalysts containing 1% and 10% of water, respectively, gave 199 and 192% yields of alkylate; hydrogen fluoride containing 26% of water produced *s*-butyl fluoride and almost no alkylate.

Activity of the catalyst is also decreased by dilution with nonaqueous substances such as hydrocarbons in the catalyst sludge (Linn and Grosse, 19). The effect is smaller than that of dilution with water and the catalyst remains active until the hydrogen fluoride concentration drops below about 80%. In typical commercial operation, fresh (recycled) catalyst contains 85–90% titratable acid, about 1.5% water, the remainder being the highly unsaturated hydrocarbons in the catalyst complex.

As has already been mentioned, alkylation in the presence of hydrogen fluoride may be carried out over a wide range of temperature. In the alkylation of isobutane with isobutylene, for example, increasing the reaction temperature from -24° to $+32^{\circ}$ had little effect on either the yield (198 and 195%, respectively) or the quality (91.5 and 92.0 A.S.T.M.

octane number, respectively) of the product (Linn and Grosse, 19). Further increase in the temperature to 60° caused a decrease in the yield of alkylate (177%) and an increase in the amount of destructive alkylation; the octane number of the alkylate was 89.0.

Other variables may also be changed over a rather wide range without any marked effects. Suitable conditions, as exemplified by those used in commercial plants, include volume ratios of catalyst to hydrocarbon ranging from about 0.5 to about 1.5, and mole ratios of isoparaffin to olefin ranging from about 5 to about 10. The contact time may be as low as one-half minute or as high as several hours; contact times of about 15 to 30 minutes are used in commercial operation. Branched chain paraffins undergo isomerization and decomposition on long contact with hydrogen fluoride (Linn, 42; cf. Webb and Gallaway, 43).

The alkylations are carried out under sufficient pressure (usually about 100–150 p.s.i.) to keep the major portion of the hydrocarbon in the liquid phase.

The composition of the alkylates obtained by the reaction of isobutane with pure olefins at relatively low temperatures indicates that it is possible to obtain products which consist largely of the primary products, that is, those of molecular weight equal to the sum of the molecular weights of the isoparaffin and the olefin. Such "selective alkylation" of isobutane occurred in batch experiments carried out at 10° using an isoparaffin to olefin mole ratio of about 3 and a catalyst to hydrocarbon volume ratio of about 0.15 (Linn and Grosse, 19). The alkylate obtained with propene contained 50% heptane consisting largely of 2,3-dimethylpentane together with a smaller amount of 2,4-dimethylpentane; about 10% 2,2,4-trimethylpentane was also present. Alkylation with 1-butene, 2-butene, and isobutylene, respectively, resulted in alkylates, the distillation curves of which were very similar. About 80% of the alkylate consisted of octanes. In the case of the two *n*-butylenes, this was roughly half 2,2,4-trimethylpentane; the remainder consisted of the octanes boiling at 110–114°, 2,3,4-trimethylpentane being the largest single component. In the case of isobutylene, about two-thirds of the octane fraction was 2,2,4-trimethylpentane. The aviation gasoline cuts (150° end point) of the 1-butene, 2-butene, and isobutylene products were 92.7, 95.3, and 96.7, respectively. Explanation of the fact that the *n*-butylene products were so similar has already been given (Section II).

Unpublished results (Linn, 42) indicate that still more selective alkylation of isobutane occurs at lower temperature, –20 to –30°.

Alkylation of isopentane with propene at 10° resulted in a 272% yield of liquid alkylate by weight of the olefin; 19% of isobutane was also formed (Linn and Grosse, 19). The yield of alkylate (the theoretical is 272%) and

the fact that only 26% of the alkylate boiled in the octane range indicate that hydrogen transfer and destructive alkylation reactions occurred.

As in the case of the sulfuric acid products, a large number of commercial hydrogen fluoride alkylates were investigated during World War II in order to correlate yields, octane numbers, and compositions of the aviation gasolines produced (Glasgow *et al.*, 40; Field and Gould, 41; Webb and Gallaway, 43). A detailed discussion of the results and their significance can not be presented here. It will suffice to indicate that it was found that the hydrogen fluoride alkylates were quite similar to the sulfuric acid products except for a higher content of 2,2,4-trimethylpentane. An alkylate obtained by the reaction of isobutane with propene in the presence of hydrogen fluoride contained 16.5% by volume 2,2,4-trimethylpentane and 41% heptanes and had an A.S.T.M. octane number of 87.5 (Glasgow *et al.*, 40, Field and Gould, 41); another product contained 19% 2,2,4-trimethylpentane and 56% of heptane and had an octane number of 89.7 (Webb and Gallaway, 43). An analogous sulfuric acid alkylate contained 8% 2,2,4-trimethylpentane and 65.5% heptanes and had an octane number of 88.7 (Glasgow *et al.*, 40; Field and Gould, 41). It may be concluded that more side reaction, namely hydrogen transfer, occurred in the presence of hydrogen fluoride.

Similar differences were observed with alkylates prepared by the reaction of isobutane with butylenes (Glasgow *et al.*, 40; Field and Gould, 41). Thus, a hydrogen fluoride alkylate having an A.S.T.M. octane number of 91.1 contained 41.7, 2.9, 9.4, and 10.0% (total, 64.0%) 2,2,4-, 2,2,3-, 2,3,4-, and 2,3,3-trimethylpentane, respectively. An analogous sulfuric acid product contained 26.8, 1.6, 19.2, and 14.9% (total, 62.5%) of the respective trimethylpentanes; its octane number was 92.3.

b. With Alkyl Fluorides. Alkyl fluorides also serve as alkylating agents for isoparaffins in the presence of hydrogen fluoride (Linn, 20). The products are similar to those obtained when olefins are used; they contain only traces (0.01 to 0.1%) of fluorine. Batch alkylation of isobutane with isopropyl fluoride at 37° resulted in a 226% yield of alkylate by weight of the propene available from the alkyl fluoride; heptanes and octanes were present to the extent of 41 and 29%, respectively, by weight of the alkylate. Alkylation of isopentane with isopropyl fluoride under the same conditions resulted in a 247% yield of alkylate containing 23% octanes and 42% decanes and higher boiling product; hydrogen transfer and destructive alkylation occurred to a large extent.

Alkylation of isobutane with *s*-butyl fluoride produced a 206% yield (by weight of the butene available from the alkyl fluoride) of alkylate, the composition of which did not differ significantly from that of the alkylate

obtained when 2-butene was used as alkylating agent. The theoretical implications of this observation are discussed on p. 38.

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Surface Area Measurements

A New Tool for Studying Contact Catalysts*

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I. INTRODUCTION

Recently on reviewing the various five-year periods of development in catalysis between the two World Wars, Taylor (1) stated: "The final five-year period (1935-1940) of our survey gave to contact catalytic science a tool of which it had long been in sore need." He was referring to a new method that had been worked out for measuring the surface areas of catalysts or other finely divided or porous solids by means of the physical

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adsorption of gases close to their boiling points. In describing the experimental procedure involved, he continued: "The technique is a standardized one which can be reproduced by different workers in different laboratories with considerable accuracy and reproducibility. It, therefore, becomes a norm for expressing numerically what many believe to be very close to the accessible surface of a solid body." He went on to express the hope that such surface area determinations would become a required part of all catalyst publications and catalyst patent applications.

In view of the general importance that seems likely to be attached to this new tool for measuring catalyst surface areas, it seems worthwhile to restate occasionally its details and to discuss critically new developments in its theory and application in catalytic work. Accordingly, in the present chapter there is first presented a review of the gas adsorption method as originally developed and published, and then a critical discussion of recent papers dealing with its new modifications, derivations, and applications to catalysts and catalytic materials.

II. MEASUREMENT OF SURFACE AREAS BY LOW TEMPERATURE ADSORPTION ISOTHERMS

1. *History of Method*

The general idea of measuring the surface areas of catalysts by adsorption methods is not new. The earliest attempts, however, made use of chemisorption rather than physical adsorption. For example, Benton (2) attempted to measure the surface area of platinum catalysts by the chemical or activated adsorption of CO and H₂; de Boer and Dippel (3) suggested measuring the surface area of CaF₂ crystals by the chemisorption of water vapor; and Emmett and Brunauer (4a) found it possible to estimate the iron surface of a catalyst by the low temperature chemisorption of CO at -195° C. However, all methods employing chemisorption are subject to the grave limitation of finding a gas which can be shown to be chemisorbed by the entire surface rather than by a fraction of the surface of the catalyst without, however, reacting with more than a single outer layer of catalyst atoms or molecules.

Physical adsorption has long been known and in a general way has been recognized as a means of obtaining some idea as to the relative surface areas of solid materials. For example, Russell and Taylor (5) compared promoted and unpromoted nickel catalysts by noting the relative amounts of CO₂ adsorbed by them at -78° C. However, physical adsorption, like chemical adsorption, to be effective in measuring surface areas must be used in such a way as to enable one to be sure that he can determine the amount of gas required to form a complete monolayer on the solid adsorbent.

Only within the last 15 years has serious attention been directed toward ascertaining ways and means of selecting on physical adsorption isotherms the point corresponding to the amount of gas required to form a monolayer on catalysts or other adsorbents.

About 15 years ago, it became increasingly evident that a method was needed to measure the surface areas of iron synthetic ammonia catalysts in an effort to differentiate between promoter effects which merely involved the maintenance of a large surface area and those which increased the activity per unit amount of area. The method had to be applicable to active catalysts without destroying or altering their activity. It occurred to the author that a suggestion in a paper by Benton and White (6) might furnish a clue to a possible procedure for making such measurements. On obtaining an S-shaped adsorption isotherm for nitrogen on an iron catalyst at -191.5°C . they had pointed out that the rather sharp break at about 120 mm. pressure might mark the completion of a first layer and the beginning of a second layer of adsorbed gas. Clearly, if the point on such an isotherm corresponding to the completion of a monolayer of adsorbed gas could be found, a simple multiplication of the number of molecules in the layer by the cross-sectional area of the molecules being used as adsorbate would yield an absolute value for the surface area. Accordingly, the adsorption isotherms for a number of gases in the neighborhood of their boiling points were measured on an iron synthetic ammonia catalyst. The first group of results obtained (Emmett and Brunauer, 4a) is shown in Fig. 1. These isotherms marked the launching of a research program that culminated in a simple and effective method for measuring the surface area of catalysts or other finely divided or porous materials.

2. "Point B" Selection

A cursory examination of the isotherms in Fig. 1 showed that the sharp break found by Benton and White was absent. The disappearance of this break resulted from applying perfect gas corrections to the gas phase of the adsorbate gas in the adsorption bulb at liquid air temperatures. However, the corrected isotherms still seemed to contain a point that might well be related to the completion of a monolayer. All of them were characterized by a long linear portion extending usually over several hundred millimeters pressure. Furthermore, gases having molecules of approximately the same size all showed linear portions beginning at approximately the same volume of adsorbed gas. It seemed reasonable, therefore, to conclude that for the gases tried, the long linear part of the isotherm might represent the building up of a second layer of adsorbed gas. On this basis, the beginning of the long linear part of the isotherms of the type shown in Fig. 1 would represent the point of completion of a monolayer; for convenience, it was labeled

"point B." A series of adsorption isotherms for nitrogen, argon, carbon dioxide, carbon monoxide, and oxygen at low temperatures on iron and also on a variety of other finely divided or porous solids yielded a number of types of evidence recounted elsewhere (Emmett and Brunauer, 4a and b;

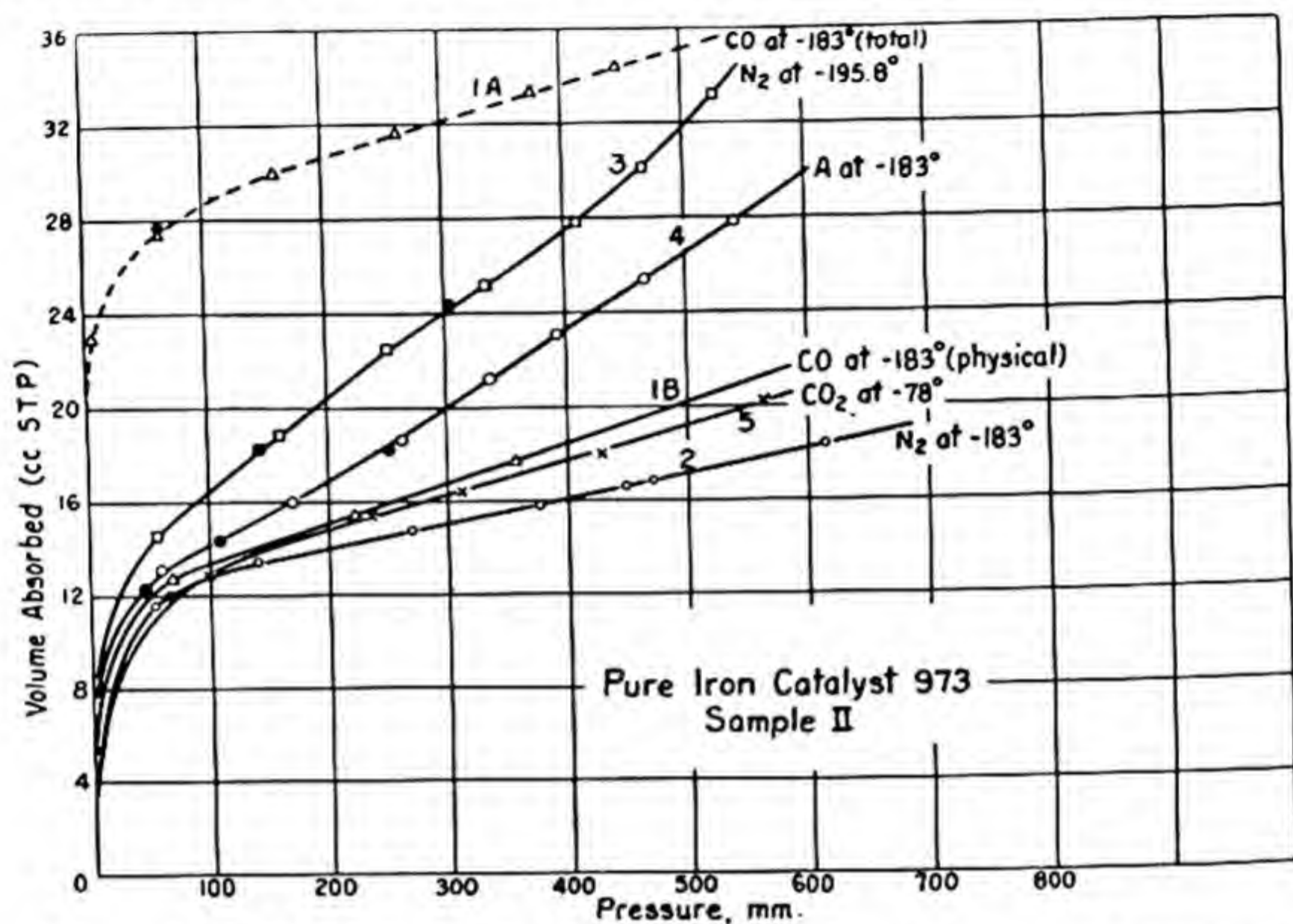


FIG. 1. Adsorption isotherms on iron catalyst (No. 973) for various gases near their boiling points (4a). Curve 1A is for the total CO adsorption at -183°C . Curve 1B represents the adsorption obtained at -183°C . after evacuating at -78°C . the sample for which the isotherm 1A had been obtained. Solid symbols are for desorption.

Emmett, 28, 33) that added to the conviction that the "point B" method could be used for these gases to measure the surface areas of contact catalysts provided the measurements were made at temperatures close to the boiling points of the respective adsorbates. However, similar adsorption experiments with butane soon showed that for many isotherms the "point B" method was inapplicable. Such a curve for butane is shown in Fig. 2, together with isotherms of other gases. Clearly it would be nearly impossible to select a "point B" on an isotherm that is so nearly a straight line through the origin as is the butane curve.

3. Derivation of the Brunauer, Emmett, Teller (γ) (B.E.T.) Equation

In view of the apparent failure of the "point B" method to cover all adsorbates and adsorbents, an attempt was made to develop a theory for the multilayer adsorption that might enable one to select the point on

adsorption isotherms corresponding to a monolayer even for gases which yield isotherms of such a shape as not to be amenable to the "point B" method. This resulted in the derivation of an equation known as the Brunauer, Emmett, Teller (7) equation that can be used to evaluate V_m ,

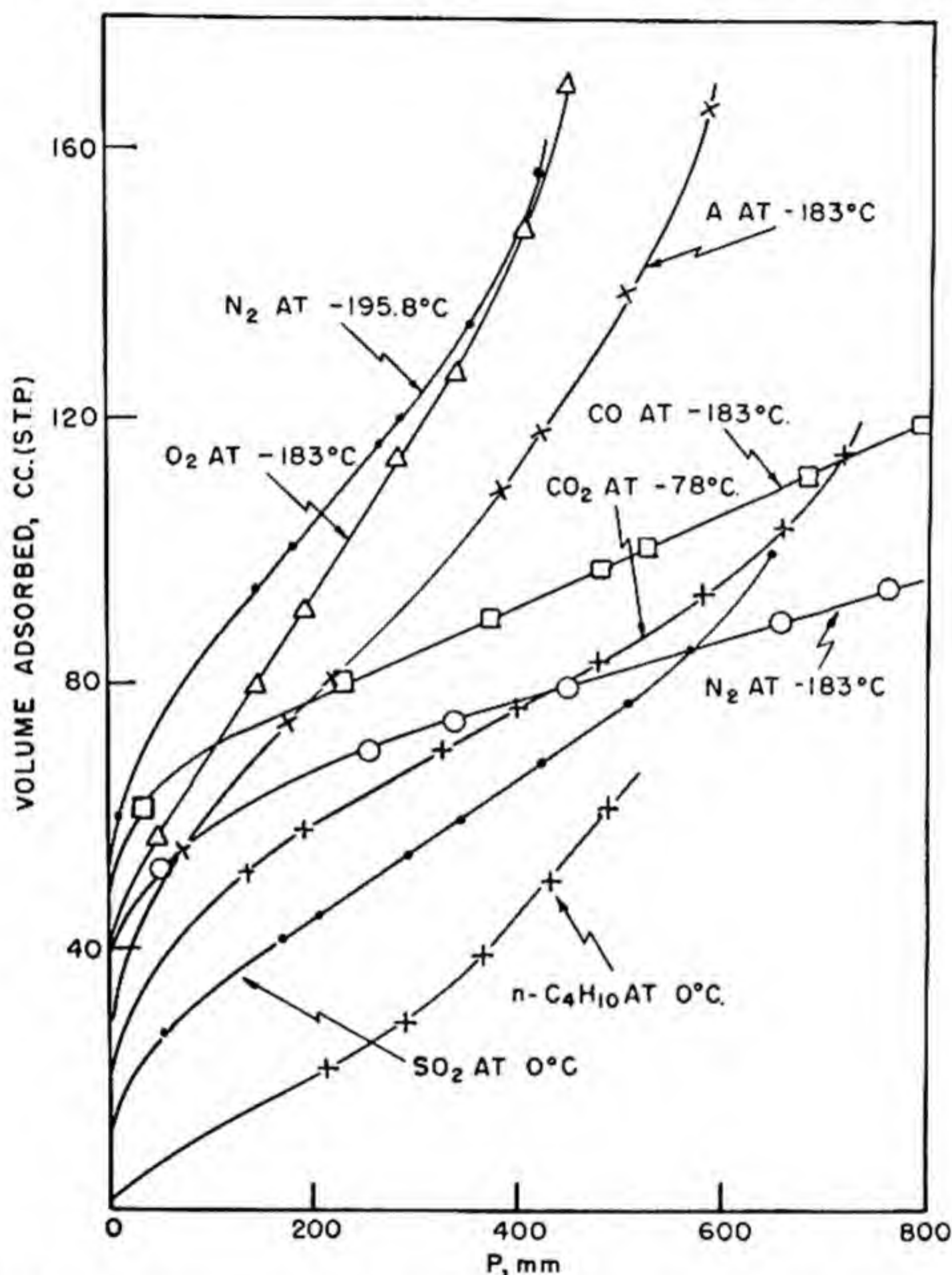


FIG. 2. Low temperature adsorption isotherms on 0.606 g. silica gel (4a).

the volume of gas in an adsorbed monolayer on the adsorbent. This equation has proved to be widely applicable in measuring the surfaces of catalysts by a variety of adsorbed gases and will now be briefly described.

Originally the B.E.T. equation was derived by a kinetic approach similar to that used by Langmuir (8) in developing his monolayer adsorption equation. Indeed, Langmuir (9) also envisioned the possibility of

multilayer adsorption but did not actually carry through the derivation of a multilayer equation. By letting s_0, s_1, s_2 , etc., represent the values for the absolute surface area covered by 0, 1, 2, etc., layers of adsorbed molecules respectively, a series of equations was obtained (Brunauer, Emmett, and Teller, 7) of the form

$$a_1 p s_0 = b_1 s_1 e^{-E_1/RT} \quad (1)$$

$$a_2 p s_1 = b_2 s_2 e^{-E_2/RT} \quad (2)$$

$$a_3 p s_2 = b_3 s_3 e^{-E_3/RT} \quad (3)$$

$$\text{and } a_i p s_{i-1} = b_i s_i e^{-E_i/RT} \quad (4)$$

where $E_1, E_2, E_3, \dots, E_i$ are the heats of adsorption in the indicated multilayers; a_1, b_1, a_2, b_2 , etc. are constants; and p is the pressure of the gaseous adsorbate. The surface area of the adsorbent is then given by the equation

$$A = \sum_0^{\infty} s_i \quad (5)$$

and the total volume of gas adsorbed by the equation

$$V = V_0 \sum_0^{\infty} i s_i \quad (6)$$

where V_0 is the volume of gas required to cover 1 sq. cm. of the surface with a unimolecular layer. It then follows that

$$\frac{V}{A V_0} = \frac{V}{V_m} = \frac{\sum_0^{\infty} i s_i}{\sum_0^{\infty} s_i} \quad (7)$$

where V_m as defined above, is the volume of gas required to form a monolayer over the entire catalyst surface.

The summation in eq. (7) can be carried out as indicated in the original paper if one makes the simplifying assumptions that $E_2 = E_3 = \dots = E_i$ and that the ratio of the coefficients for desorption and adsorption in the multilayers, $b_2/a_2, b_3/a_3$ etc. are equal to each other. The summation finally leads to the equation

$$\frac{x}{V(1-x)} = 1/V_m C + \frac{(C-1)x}{V_m C} \quad (8)$$

where x is the relative pressure, p/p_0 , at which a particular volume of gas V (expressed as cc. S.T.P.) is adsorbed by the catalyst. Clearly a plot of the left side of the equation against x permits the slope and intercept to be used

for the evaluation of the constant C and of V_m . The constant C is really equal to $\frac{a_1 b_2}{a_2 b_1} e^{\frac{E_1 - E_L}{RT}}$ where $E_1 - E_L$ is the difference between the average heat of adsorption in the first layer and the heat of liquefaction of the adsorbate. A few typical examples of the use of the equation are shown in Fig. 3 in which the isotherms from Fig. 2 are replotted, according to the

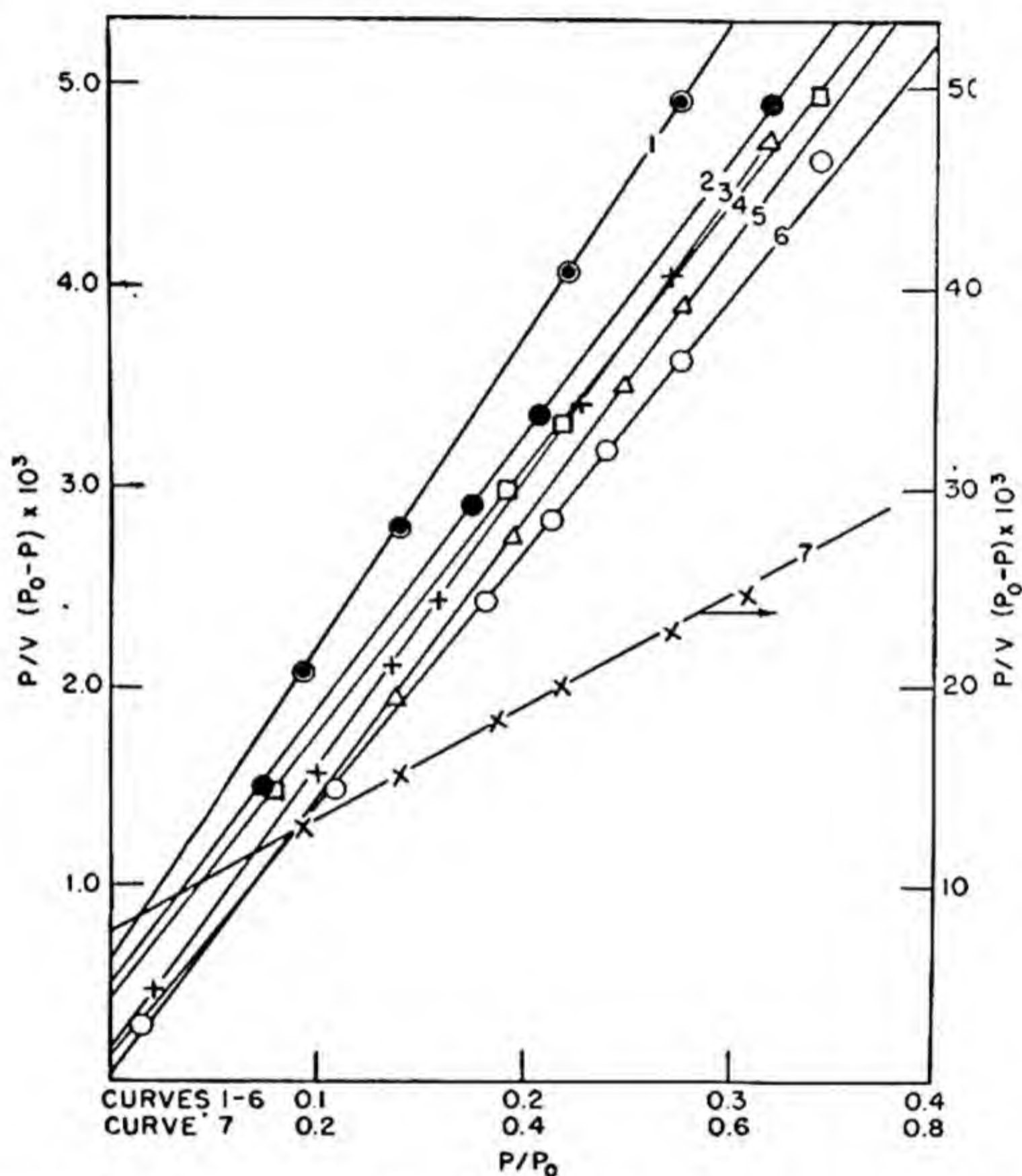


FIG. 3. B.E.T. plots (7) for the adsorption of various gases on 0.606 g. silica gel (eq. 8). Curve 1, carbon dioxide at -78° ; 2, argon at -183° ; 3, nitrogen at -183° ; 4, oxygen at -183° ; 5, carbon monoxide at -183° ; 6, nitrogen at -195.8° ; and 7, butane (C_4H_{10}) at $0^\circ C$.

multilayer B.E.T. equation. Linear plots are obtained over the relative pressure range extending from about 0.05 to 0.35 when eq. (8) is applied to the adsorption of nitrogen on the synthetic ammonia catalysts.

4. Some Advantages of the B.E.T. Equation

The first test to which eq. (8) was subjected was a comparison between V_m values for nitrogen adsorption isotherms obtained by the equation, and those estimated by the "point B" method. Table I shows the results of such a comparison (Brunauer, Emmett, and Teller, 7). It is obvious that for nitrogen isotherms the agreement between the two methods of obtaining V_m is good. In fact, it is probably well within the error involved in selecting "point B" on an experimental isotherm.

TABLE I

*Values of Constants for Adsorption of Nitrogen
at 90.1°K. on Various Adsorbents*

Substance	V_m cc./g.	Point B cc./g.
Unpromoted Fe catalyst 973 I	0.13	0.12
Unpromoted Fe catalyst 973 II	0.29	0.27
Fe-Al ₂ O ₃ catalyst 954	2.86	2.78
Fe-Al ₂ O ₃ catalyst 424	2.23	2.09
Fe-Al ₂ O ₃ -K ₂ O catalyst 931	0.81	0.76
Fe-Al ₂ O ₃ -K ₂ O catalyst 958	.56	.55
Fe-K ₂ O catalyst 930	.14	.12
Fused Cu catalyst	.05	.05
Commercial Cu catalyst	.09	.10
Cr ₂ O ₃ gel	53.3	50.5
Cr ₂ O ₃ glowed	6.09	6.14
Silica gel	116.2	127.0

Application of eq. (8) to the adsorption isotherms for butane on silica gel showed one of the several ways in which the B.E.T. equation is superior to and more useful than the "point B" concept. As illustrated in Fig. 2 the adsorption isotherm for butane on silica gel is of such a shape as to make the picking of a point corresponding to a monolayer by the "point B" method very difficult if not impossible. Yet, the data when plotted according to eq. (8) yield a value for the surface area of the gel of 383 sq. meters/g. compared to a value of 477 sq. meters/g. obtained by nitrogen at -195° C.

One further advantage of the B.E.T. equation over the "point B" method should perhaps be pointed out in passing. In Fig. 3 it can be seen that the intercept for the plots for nitrogen adsorption are quite small. Accordingly, only a small change in the slope of the linear plot would be required to make the curve pass through the origin. Hence, the possibility exists of taking only a single adsorption point in the range 0.2-0.3 relative pressure and connecting this point on a B.E.T. plot with the origin. The slope of this line should, for an adsorbent for which the nitrogen adsorption

isotherm is the normal S-shaped variety, yield a surface area value that will, as a rule, be too small by only about 1–5%. This clearly means a big advantage over the "point B" method since the latter necessitates the obtaining of sufficient adsorption points to demarcate clearly the linear part of the isotherm.

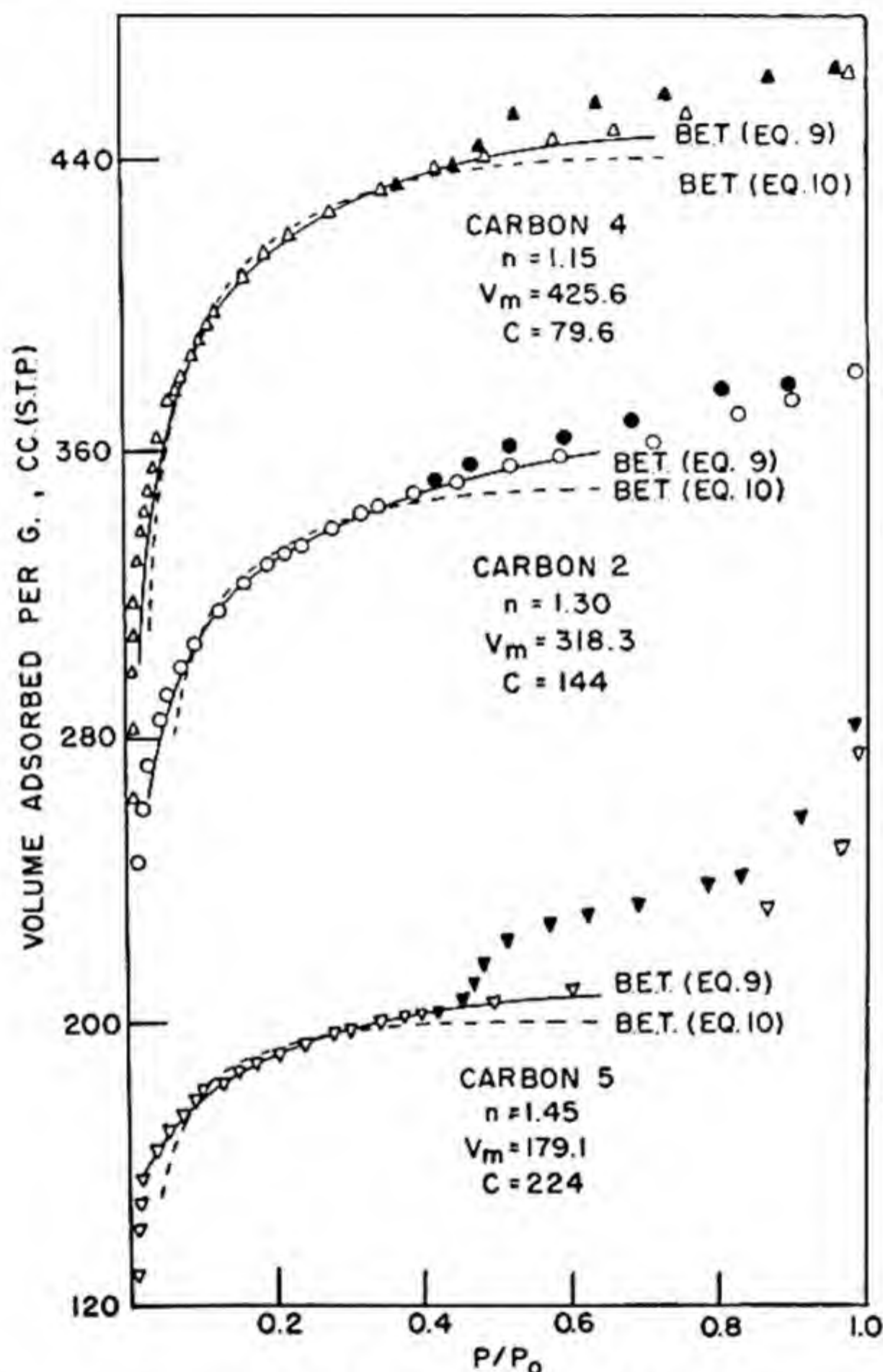


FIG. 4. Adsorption isotherms for nitrogen at -195°C . on three samples of charcoal. The curves corresponding to the " n " form of the B.E.T. equation (eq. 9) and to the Langmuir form (eq. 10) are shown for comparison. The n , C , and V_m values as well as the data are taken from the paper of Joyner, Weinberger, and Montgomery (10).

5. The B.E.T. Equation for Narrow Capillaries

In deriving eq. (8), the authors (7) assumed that the summation indicated in eq. (7) could be carried out to infinity. Clearly, however, there

might be many reasons for having to limit the summation to n layers. For example, if a capillary with plane parallel walls $2n$ molecular diameters apart is exposed to a gas at a temperature at which multilayer adsorption could occur, no more than n layers on an average could be built up on each

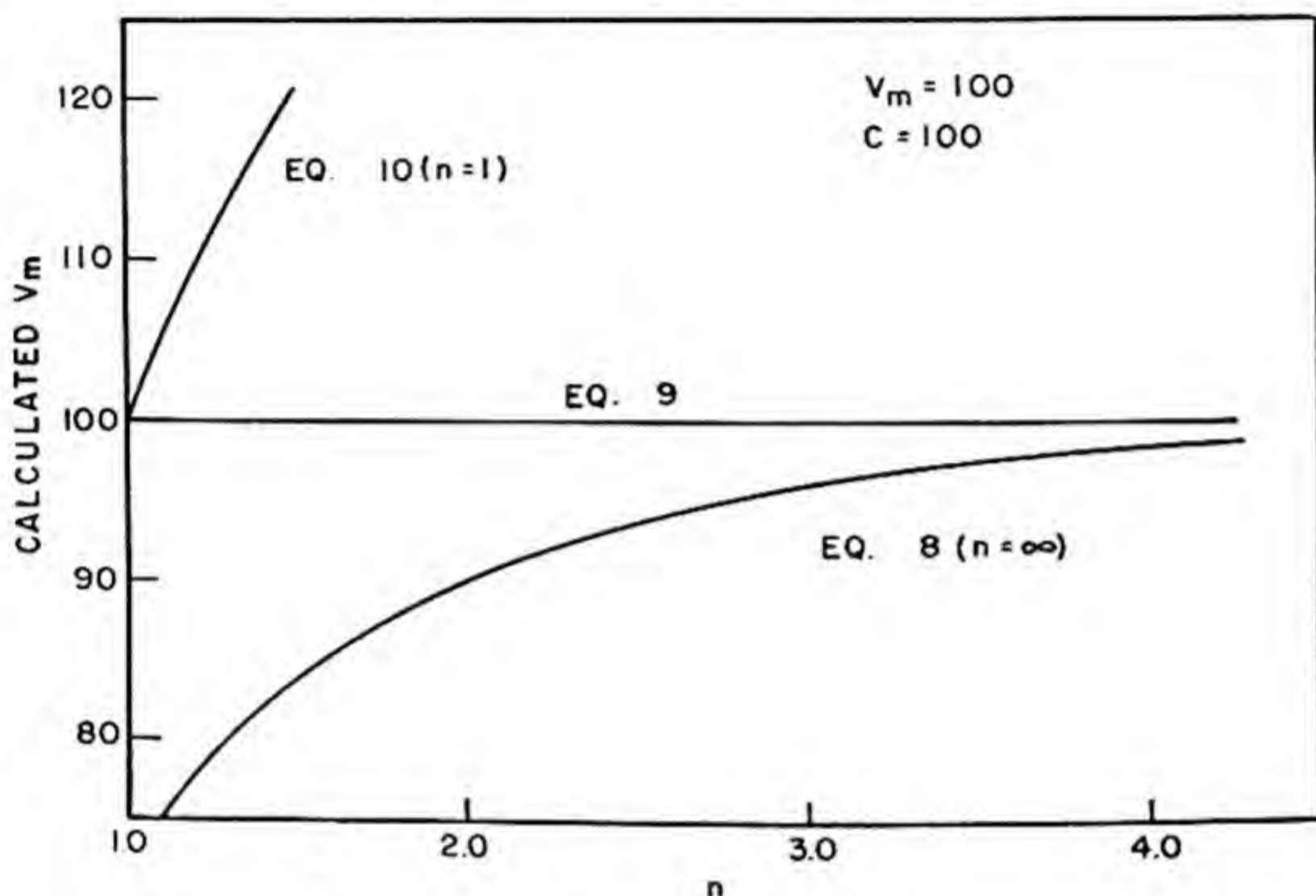


FIG. 5. Error involved in using eq. (10) and (8) as approximations for eq. (9) at various values of n . The figure was taken from the paper by Joyner, Weinberger, and Montgomery (10).

face of the capillary. To take such a case into account, the original fundamental assumptions were modified by summing to " n " layers rather than to an infinite number of layers. There was then obtained the equation

$$V = \frac{V_m C x (1 - (n+1)x^n + nx^{n+1})}{(1-x)(1 + (C-1)x - Cx^{n+1})} \quad (9)$$

where all of the symbols are the same as in eq. (8) and n is the maximum number of layers of adsorbate that could be built up on the wall of a capillary without meeting a similar layer from the opposite wall.

One interesting property of eq. (9) comes to light if one lets $n=1$. It can be shown (7) that with such an assumption the equation reduces to the form

$$p/V = p_0/CV_m + p/V_m. \quad (10)$$

This is identical to one of the forms in which the Langmuir equation can be written except that the empirical Langmuir constants are replaced by the more readily definable constants V_m , p_0 and C .

Equation (9) is much more difficult to apply than is eq. (8). However,

Joyner, Weinberger, and Montgomery (10) have shown a method by which, without too much labor, one can evaluate C , V_m , and n for materials in which the capillaries are so narrow as to force one to use eq. (9) rather than eq. (8). The details of their method need not be discussed here since they are well explained in their original paper. However, in Fig. 4 are shown several curves for the adsorption of N_2 on charcoal together with the values for n , C , and V_m obtained by them (Joyner, Weinberger, and Montgomery, 10).

They not only outline the method for applying eq. (9) but point out the percentage difference in the value of V_m that is obtained by using either of the two extreme eq. (8) or (10) for isotherms for which n is really intermediate between 1 and 5. Figure 5 is their plot of the error involved in using the simplified equations as a function of the value of n . For example, if n is really 1.5 but is assumed to be 1 in order to use eq. (10), the calculated surface area will be too large by about 15%. On the other hand, if for such an adsorbent the area is evaluated by use of eq. (8), it will be too small by about 18%. With the help of eq. (9) and the procedure they outlined it becomes possible to evaluate the surface area even of catalysts having pores so small as to render impracticable the use of eq. (8).

6. Other Methods for Measuring Surface Areas by Gaseous Adsorption

a. Procedure of Askey and Feachem (11). Several other methods for measuring surface areas with the help of gaseous adsorption isotherms have been published. Askey and Feachem (11) pointed out in an article published in 1938 that for several years they had been using low temperature adsorption isotherms for measuring the surface areas of finely divided materials. Their method is substantially the same as the first suggestion of Brunauer and Emmett (12) according to which it was postulated that an extrapolation of the linear part of the S-shaped adsorption isotherm to zero pressure should yield a value for the volume of gas required to form a monolayer. A simple multiplication of the number of molecules in this monolayer by the average cross-sectional molecular area would then yield an absolute surface area. This method was later judged by Emmett and Brunauer (4a) to be less accurate and more open to question than the "point B" method; it certainly is less well founded than the method (7) using eq. (8). On the other hand, it must be admitted that this zero pressure extrapolation method certainly will yield areas which are of the correct order of magnitude and which are probably capable of yielding fairly reliable relative areas for various finely divided solids.

b. Work of Harkins and Jura (13). A distinctly different approach to the interpretation of low temperature gas adsorption isotherms has been followed by Harkins and Jura (13). By assuming that the same type of

equation is applicable to the adsorption of gases on solids that has been found applicable for correlating the surface spreading force of adsorbed films on liquids with the area occupied per adsorbed molecule, they have been able to obtain the equation

$$\log p = B - A/V^2 \quad (11)$$

where V is the volume of gas adsorbed at pressure p and A and B are constants. Furthermore, they deduce that the area of a solid can be obtained from a plot of $\log p$ vs. $1/V^2$ by means of the equation

$$\text{Area} = k(S)^{1/2} \quad (12)$$

where S is the slope of the plot of eq. (11) and k is a constant that had to be evaluated by some independent means. In some very ingenious experiments they (Harkins and Jura, 14, 15) also provided an independent means for evaluating k . By exposing a finely divided solid such as TiO_2 to a sufficient pressure of water vapor to form four or five statistical adsorbed layers and then immersing this water vapor coated sample in liquid water, they were able to obtain from the evolved heat a direct measure of the surface area of the powder without any assumption as to the molecular cross-section of the water molecule. They merely divided the heat evolved on immersing the sample by 118.5 ergs, the value for the normal surface energy per square centimeter of liquid water, to obtain a value for the number of square centimeters of area in the sample. Using this surface area for the powder they were then able to evaluate the constant k of eq. (12). For other solids they could apply eq. (12) directly by assuming that the constant k was independent of the type of surface. Proceeding in this way, they obtained the surface area of six separate solids from their nitrogen adsorption isotherms and compared them with the areas that were obtained by plotting the adsorption data according to eq. (8). The results are shown in Table II. Comparison of the values in column 2 with those in column 6 of Table II shows that the agreement between the two independent methods of interpreting the nitrogen isotherms is clearly remarkable and serves to strengthen the general conviction that gaseous adsorption isotherms can be used to obtain reliable surface area values for catalysts and other finely divided materials.

Several papers (Livingston, 16; Emmett, 17) have been written to try to explain the queer coincidence that such divergent interpretations of the low temperature adsorption isotherms should lead to the same surface area values for the adsorbents. The agreement is still very puzzling and cannot be said to have been satisfactorily explained. However, attention has been called to the fact (17) that apparently the good agreement indicated by the nitrogen data in Table II is not always obtained. As a matter of fact it seems to be true that only when the C value of eq. (8) is about 100 will the

area values obtained by eq. (8) and by eq. (11) and (12) of Harkins and Jura (13) agree. Nevertheless, since many gases (especially those boiling near -190°C.) yield C values in the range between 50 and 150, the agreement between the two methods is for the most part very satisfactory. Indeed, it is not yet possible to tell which method gives the more reliable area for those materials in which a divergence (which incidentally never exceeds 30 or 40%) between the two methods exists.

TABLE II

Areas_a of Solids Calculated by the New Method of Harkins and Jura and by that of Brunauer, Emmett and Teller^b

Solids	New method of Harkins and Jura				B.E.T. method				
	N ₂	H ₂ O	<i>n</i> -Bu- tane	<i>n</i> -Hep- tane	N ₂ 16.1 Å. ²	H ₂ O 14.8 Å. ²	H ₂ O 11.3 Å. ²	<i>n</i> -Bu- tane 56.6 Å. ²	<i>n</i> -Hep- tane 64.0 Å. ²
TiO ₂ (Standard)	13.8	13.8	13.8	13.8	13.8	13.8	10.5	13.8	13.8
TiO ₂ II	8.7	8.4		8.7	8.6	11.7	8.8		8.7
SiO ₂ (Quartz)	3.2	3.3		3.3	3.2	4.2	3.2		3.6
BaSO ₄	2.4	2.3	2.2	2.3	2.4	2.8	2.1	2.7	2.4
ZrSiO ₄	2.9	2.7			2.8	3.5	2.7		
TiO ₂ +Al ₂ O ₃	9.6	11.8			9.5	12.5	9.5		

^a Areas in sq. meters/g.

^b Table III, Harkins and Jura, *J. Am. Chem. Soc.* 66, 1366 (1944) with a column of calculations for the areas by B.E.T. method using water isotherms with an assumed cross-section of 11.3 Å.² for the water molecule.

c. Gregg's Proposed Method. Gregg (18) has suggested a method very similar in theory to that developed by Harkins and Jura. It has, however, been applied for the most part only to charcoal and similar adsorbents having a very fine pore structure, and not, as yet, to materials for which an independent method of surface area appraisal is possible. It is quite probable, however, that his method when applied to low temperature nitrogen adsorption isotherms will yield surface areas in general agreement with those deduced by the B.E.T. or the Harkins and Jura plots.

III. LIMITATIONS AND GENERAL CRITIQUE OF THE GAS ADSORPTION METHODS

1. Molecular Size

In their original paper, Emmett and Brunauer (4a) suggested obtaining cross-sectional molecular areas for the various adsorbates by means of the equation

$$\text{Molecular Area} = (4) (0.866) \left(\frac{M}{4(2)^{1/2} Ld} \right)^{2/3} \quad (13)$$

where M is the molecular weight of the adsorbate, L is Avogadro's number and d is the density of the solidified or liquefied adsorbate. This equation was derived on the assumption that the molecules have cross-sectional areas equivalent to those possessed in the liquid or solid forms and that they are close packed on the surface of the adsorbents. Experience has shown that, whereas this procedure gives very satisfactory agreement between areas obtained by molecules having similar boiling points (such as, for example, nitrogen, argon, carbon monoxide, or oxygen) it yields areas for other adsorbate molecules that may be as much as 50% smaller than those obtained by using nitrogen as adsorbate. Thus, the general conclusion drawn from work of Beebe, Beckwith, and Honig (20) from measurements with krypton is that a correction factor of about 1.3 has to be used to bring the area as measured by krypton up to the area as measured by nitrogen, provided the cross-section of the krypton atoms is obtained by applying eq. (13) to liquid krypton. Davis, De Witt, and Emmett (19) have similarly shown that correction factors of this same magnitude (1.2–1.5) have to be used to bring into agreement the areas as determined by butane, Freon 21 (CHCl_2F), or butene with those obtained by nitrogen. The reason for this discrepancy is not as yet known. It seems that for some unexplained reason the molecules of these various adsorbates appear to have larger molecular areas than those calculated by eq. (13).

2. *The k Value of Harkins and Jura (13, 14, 15)*

The method of Harkins and Jura avoids this difficulty by determining from the heat of wetting experiments on TiO_2 a surface area which in turn can be used to evaluate the constant k for various adsorbates at given temperatures. By proceeding in this way they assign values of 3.83, 13.6, and 16.9, for example, to molecules of water at 25°; n -butane, at 0°, and n -heptane, at 25° C. These assignments enable them to obtain very good agreement among the area values for different adsorbates on a variety of solids. In Table II, for example, in columns 2, 3, 4 and 5 are compared the areas that they obtained for six different solids by using nitrogen, water vapor, n -butane and n -heptane as adsorbates. In Table II of one of their papers Harkins and Jura (13) have shown that the areas obtained by assigning the cross-section areas to water, butane, and heptane on the basis of eq. (13) as recommended by Emmett and Brunauer (4a) are too small by as much as 50%. Admittedly the molecular areas used by Harkins and Jura (13) produce a much better agreement for the surface area values on the different adsorbents than can be obtained by the B.E.T. method using the molecular areas obtained by eq. (13). It must be remembered, however, that the procedure of Harkins and Jura is tantamount to making the areas by nitrogen, butane, heptane, and water vapor agree on a given solid and

then applying these same relative areas to other solids. Columns 6, 7, 8 and 9 in Table II show that if a similar arbitrary procedure is followed in applying the B.E.T. method, agreement equally as good as that of Harkins and Jura can be obtained for the various adsorbates. Accordingly, if one is using an adsorbate other than nitrogen one must be prepared to find that molecular areas calculated by eq. (13) may be as much as 50% too small to yield good agreement with the results obtained from the nitrogen isotherms.

3. Modifications and Other Derivations of the B.E.T. Equation

Cassie (21), and more recently Hill (22) have found that eq. (8), the B.E.T. equation, can also be derived by a statistical thermodynamic approach. Hill (23) has in addition pointed out that the original postulates of Brunauer, Emmett, and Teller (7) that lead to the derivation of eq. (9) by a kinetic method can be shown by statistical thermodynamics to lead to the same equation. This is of interest since both Pickett (24) and Anderson (25) have suggested that the method of summation used in obtaining eq. (9) should be so altered as to produce an equation in the form

$$V = \frac{V_m C x (1 - x^n)}{(1 - x) (1 + (C - 1)x)} \quad (14)$$

in which the symbols have the same meaning as in eq. (9). Equation (14) has the advantage of leading to the conclusion that when $x = 1$, the total amount of adsorbate in the adsorbent would be nV_m rather than $\frac{(n+1)V_m}{2(1+1/Cn)}$ that would be predicted by eq. (9). Fortunately, both eq. (9) and eq. (14) agree in the range of relative pressures used in calculating surface areas. It is only at the higher values of x that they diverge. For this reason the critical comparison of eq. (9) and (14) need not in the present chapter be carried further.

4. Confirmation of B.E.T. Method on Nonporous Solids

For nonporous solids the areas obtained by using nitrogen adsorption isotherms at liquid nitrogen temperature in conjunction with "point B" method, with the B.E.T. equation or with the equations of Harkins and Jura all appear to check each other and to be in agreement with areas obtained by independent means. Space will not permit a complete listing of all comparisons that have been made by way of checking the validity of these methods involving the physical adsorption of gases. It will perhaps suffice to point out that good agreement is obtained between the gas adsorption method and areas estimated, (1) by the heat of immersion method by Harkins and Jura (13) for TiO_2 , (2) by the electron microscope photographs for carbon black (Anderson and Emmett, 26; Emmett and De Witt,

27), (3) by the direct microscopic observations on sized glass spheres 7 microns in diameter (Emmett, 28), (4) by permeability measurements on ZnO pigments using various liquids as fluids (28), (5) by ultramicroscopic observations on suspensions of these same ZnO pigments (28), and (6) by the adsorption of stearic acid and other molecules from solution on ZnO pigments (Ewing, 29). There seems to be little question that by the gas adsorption methods, reliable surface areas can be obtained for nonporous solid substances.

5. Confirmation on Large-Pore Solids

For porous solids in which the cracks, crevices and capillaries all appear to be many fold greater than molecular dimensions, there seems to be no reason for doubting the general applicability of the gas adsorption methods. It must, of course, be admitted that for such solids there are fewer methods available for obtaining independent estimates of the areas. By means of low angle scattering, however, it is possible to estimate the average particle size of gels and other porous catalysts. The few published results of such comparisons indicate that for porous solids, too, the nitrogen adsorption method gives reliable surface area values. Thus Elkin, Shull, and Roess (30) found that for a series of silica gels the particle sizes revealed by low angle scattering measurements yielded area values which were larger than the areas obtained by the nitrogen adsorption method by factors ranging from 1.14 to 1.5 for the various gels. This constitutes excellent agreement in view of the combined uncertainties of the two methods. A few data obtained by adsorption from solution may also be used to test the areas obtained by the adsorption method. Thus, Smith and Fuzek (31) found that the areas obtained by adsorbing palmitic acid from benzene on Raney nickel catalysts agreed very well with those obtained by the nitrogen adsorption method.

6. Area Measurements on Charcoal and Other Fine-Pore Solids

Only for materials giving isotherms approaching the flat Langmuir type shown in Fig. 4 does there appear to be much uncertainty relative to the surface area of the porous solid as estimated by the gas adsorption method. Obviously when pores are sufficiently close to molecular dimensions, the very definition of surface becomes rather hazy. For example, the surface of some of the smaller capillaries will probably be reached only by the smallest adsorbate molecules. Hence, the area would depend upon the size of molecule used as a measuring unit. However, even for a silica gel sample that has pores so small as to cause its nitrogen adsorption isotherm to resemble those obtained on charcoal, the x-ray low angle scattering measurements of Elkin, Shull, and Roess (30) give good agreement with the nitrogen areas. But this is about the only means available for checking

the gas adsorption method when fine pores are involved, though a few meager comparisons have been made between areas deduced by the adsorption of nitrogen at -195°C . for charcoal, and areas obtained by adsorption from solution onto the charcoal. Measurements by Lemieux and Morrison (32) on the adsorption of homologous series of acids from aqueous solution yield surface areas that are 30 to 70% lower on gas adsorbent charcoal than those estimated from the nitrogen isotherms. As pointed out above, it seems fairly certain that V_m values evaluated with the help of eq. (9) by the method of Joyner, Weinberger, and Montgomery (10) are as reliable as we know how to obtain at the present time for the surface accessible to molecules of this size.

7. Limitations and Precautions in Using the B.E.T. Method

Other limitations and characteristics of the gas adsorption surface measurements have been pointed out in detail in previous publications (Emmett, 33, 34). It will suffice here to summarize them briefly. (1) The B.E.T. surface area method using nitrogen as adsorbate is generally applicable to any porous or nonporous solid in which a sample of 5 or 10 cc. has an area of at least 1 sq. meter. (2) By using adsorbates with low p_0 values such as ethane or ethylene at liquid nitrogen temperatures, it is possible to extend the sensitivity of the method sufficiently to enable one to measure surface areas as small as 100 sq. cm. with an accuracy of about 10% (Wooten and Brown, 35). (3) The presence of a chemisorbed layer of gas on the adsorbent does not interfere with the low temperature nitrogen adsorption measurements provided, of course, that the pores are not so small that a monolayer of chemisorbed gas can block off or close up some of the tiny pores and hence actually decrease the amount of area to which the nitrogen has access. (4) In preparing the samples for measurement it is necessary to degas them at a temperature merely high enough to remove any easily condensible vapors such as water vapor which might be blocking part of the surface by being condensed in capillaries.

The detailed procedure involved in making the adsorption measurements is being omitted from this chapter because it has already been published several times (Emmett, 28, 33) and is, in addition, very little different from standard gas adsorption techniques that have been described in the literature for many years.

IV. APPLICATION OF SURFACE AREA METHODS IN THE STUDY OF SOLID CATALYSTS

1. Activity vs. Surface Area

At the outset it should be re-emphasized that the low temperature gas adsorption methods measure the total accessible surface of a catalyst

regardless of whether that surface is active catalytically. Accordingly, it does not necessarily follow that the total activity of a series of chemically similar catalysts will be proportional to the surface areas as measured, for example, by nitrogen adsorption. Deviations from proportionality could arise from two different sources. In the first place, the fraction of the surface that might be in the form of active points or active planes could well be different on one catalyst than on another that is chemically identical. In such a case, of course, the catalyst with the larger number of active points per cubic centimeter of catalyst will have the greater activity regardless of the absolute surface area as measured by adsorption methods. However, even if the surfaces of two catalysts that are being compared are completely uniform in activity and identical chemically, it still does not follow that the activities of the two catalysts will be identical. It is always possible that much of the surface on one of the catalysts is located in pores that are so small as not to be readily available to the reacting gases. It could, therefore, easily happen that a catalyst with the larger surface as judged by the nitrogen method might possess the lower activity for catalytic reactions. Both Thiele (36) and Wheeler (37) have discussed this question of the relation between pore size and the fraction of the inner surface of the catalyst that can be utilized for a particular reaction.

In spite of the above-mentioned factors that might interfere with correlations between surface areas and catalytic activity, it has often been found that a good correlation does exist. For example it has been pointed out in a paper by Owen (38) that the catalysts used in dehydrogenating butene to form butadiene have activities that are directly proportional to the total surface areas. For such materials the surface area measurements may serve as a good control for predicting the activity that will be possessed by a given catalyst.

2. Measuring Surface Promoter Distribution

Attention has already been called to the use that has been made of surface area measurements in studying synthetic ammonia catalysts. It has been possible, for example, to show that certain promoters have a specific influence on the activity per unit surface area (4). Thus iron catalysts containing both K_2O and Al_2O_3 as promoters have surfaces that are only about one-third as large as those containing only Al_2O_3 as promoter and yet are several fold more active under synthesis conditions.

Another valuable bit of information relative to promoters on iron catalysts has been made possible by the adsorption method for measuring surface areas. It has been established (Emmett and Brunauer, 39, 40) that the few per cent promoter content added to an iron catalyst actually covers as much as 50–75% of the surface of the reduced catalyst, thereby exerting

a much more marked influence on the activity of the catalyst than would be expected if the ratio of promoter atoms to iron atoms were the same on the surface as throughout the bulk of the catalyst. This observation in regard to the amount of promoter on the surface arose from the discovery that at

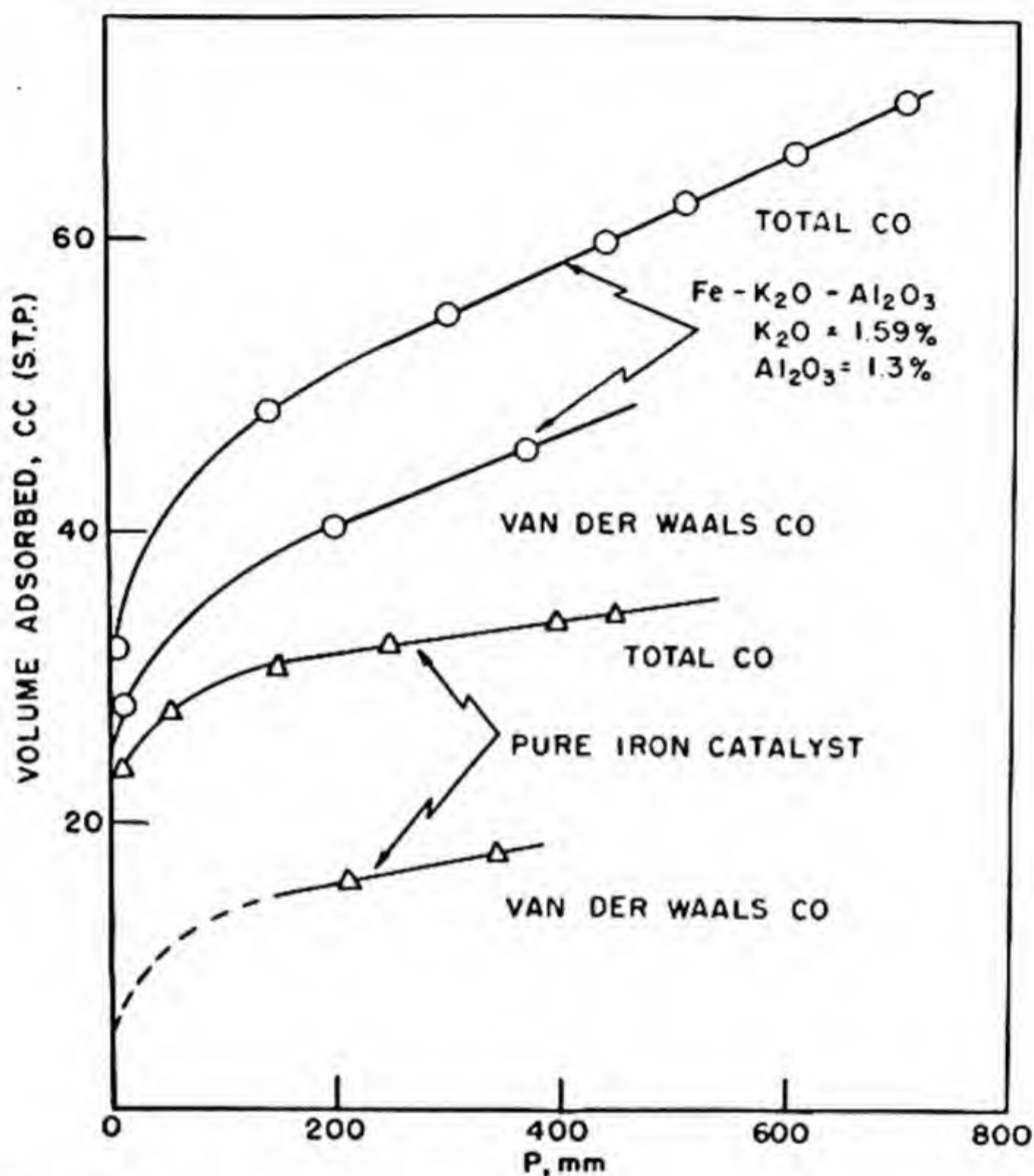


FIG. 6. Comparison of the isotherms for total carbon monoxide adsorption at -183° and for the physical adsorption on about 45 g. of pure iron synthetic ammonia catalyst (No. 973) and on a similar quantity of a doubly promoted iron catalyst (No. 931) (39).

-183° C. carbon monoxide is quickly chemically adsorbed by the surface of a pure iron catalyst in amounts sufficient to cover the entire surface (4). Accordingly, it seemed reasonable to conclude that whenever the volume of CO chemisorption on an iron catalyst promoted with Al_2O_3 and K_2O was smaller than the volume of nitrogen required to form a monolayer over the entire catalyst, one had an indication that part of the surface was being covered up by promoter molecules that were concentrating preferentially in the surface layer. For the doubly promoted catalyst, such measurements

indicated that only about 30–50% of the surface of the iron was actually in the form of free iron atoms. Isotherms leading to such a conclusion are shown in Fig. 6. Fortunately it was possible (Emmett and Brunauer, 39, 40) to substantiate this conclusion in another way. Carbon dioxide at -78°

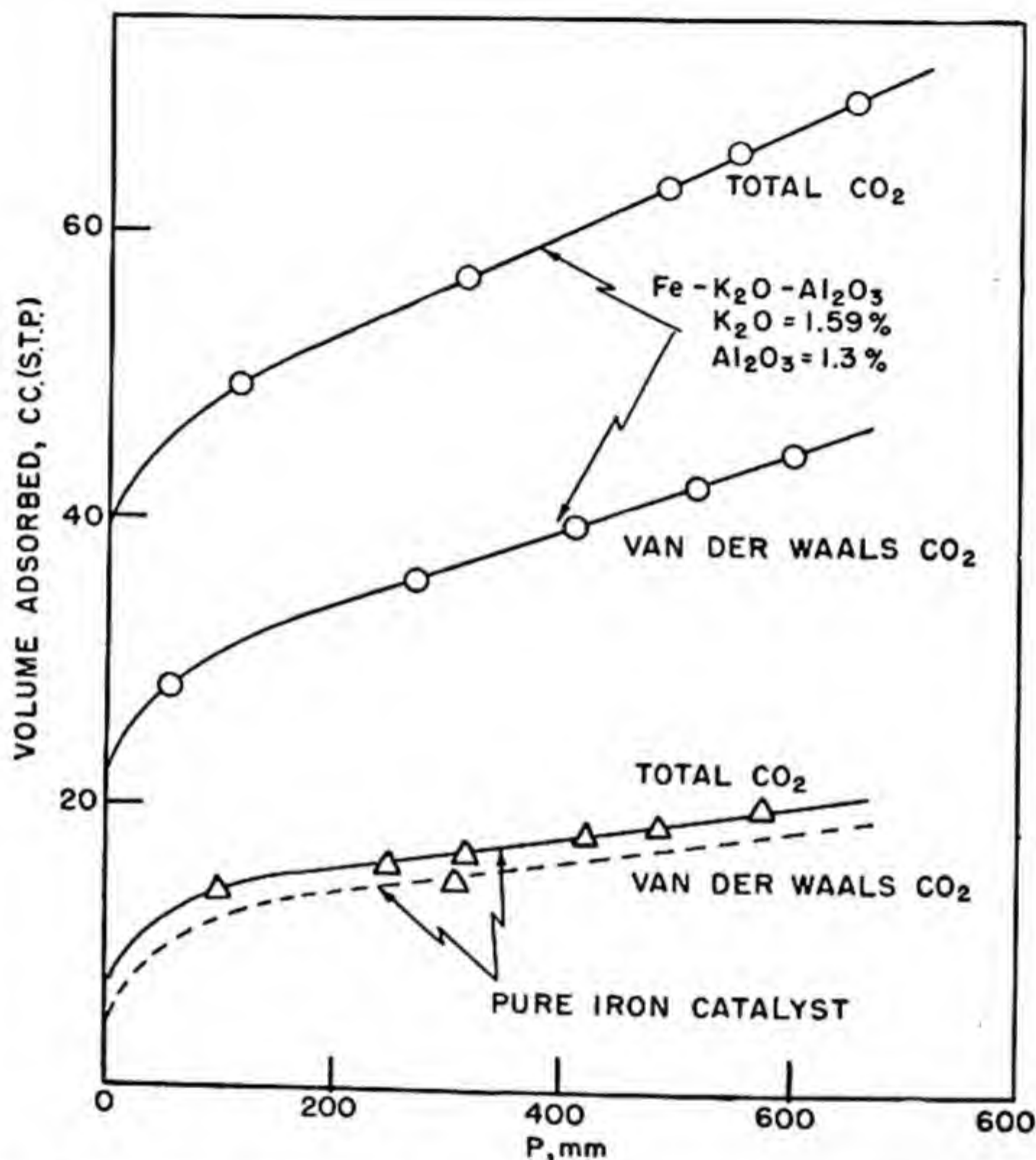


FIG. 7. Comparison of the isotherms for the total and the van der Waals adsorption of carbon dioxide at -78° on 45 g. samples of a pure iron catalyst (No. 973) and a doubly promoted iron synthetic ammonia catalyst (No. 931) (39).

is only physically adsorbed by a pure iron catalyst; however, if any alkali is present as promoter in the catalyst a considerable amount of chemisorbed carbon dioxide is taken up by the catalyst. Isotherms illustrating this effect are shown in Fig. 7. A comparison of the volume of carbon dioxide taken up by the promoter molecules on the catalyst and the volume of CO chemisorbed by the same catalyst showed that the sum of the CO chemisorption and the CO₂ chemisorption was approximately equal to the volume

of nitrogen required to form a monolayer over the entire catalyst. It, therefore, seemed reasonable to conclude that the CO was being chemisorbed by the iron atoms and that the CO₂ was being chemisorbed by the promoter molecules containing alkali. Accordingly, the combined chemisorption measurements of CO and CO₂ together with a measurement of the total surface by low temperature nitrogen adsorption afforded a means of telling what fraction of the doubly promoted iron catalyst was covered with promoter molecules and what fraction consisted of iron atoms.

3. *Area Measurements and Chemisorption*

The extension of the above described method for estimating the surface concentrations of promoters involves finding gases for the chemisorption measurements that are taken up by the principal catalyst component but not by the promoter molecules, or vice versa. This may not always be possible. Nevertheless, the results on iron catalysts are suggestive and point to a possible means of combining physical and chemical adsorption measurements to furnish more information about the composition of the surface of a catalyst than it had been possible to obtain previously. Indeed, area measurements facilitate the interpretation of all chemisorption runs on either single component or promoted catalysts. Thus Frankenburg (40a) and Davis (40b) found it convenient and helpful to know the surface area of the tungsten powder on which they were studying the activated adsorption of H₂ and N₂ respectively.

4. *Application to Fischer-Tropsch Catalysts*

Another application that has been made of surface area measurements has to do with the preparation of Fischer-Tropsch catalysts. Anderson (41) and his coworkers at the Bureau of Mines are in the process of comparing the surface areas of the reduced and unreduced cobalt and iron oxide catalysts with the activities of the final catalysts. The work is in too early a stage of development to permit any final conclusions to be drawn because many factors other than surface area may enter into the performance of Fischer-Tropsch catalysts. Nevertheless, the surface area measurements will permit the control of one of the variables that otherwise would have remained an unknown complicating factor.

Similarly, in work that has been carried out recently on the use of C¹⁴ and compounds of C¹⁴ in studying the mechanism of the Fischer-Tropsch synthesis over iron catalysts, the author and his coworkers have been guided continually by a knowledge of the surface area of the catalysts at every stage of the synthesis. Without such area measurements much of the work would have been impossible.

5. *B.E.T. Equation and Pore Size Measurements*

a. Work of Wheeler (42), of Shull (44), and of Ritter (43). Another application of surface area measurements has to do with pore size determination of porous catalysts. By assuming that the upper part of S-shaped isotherms such as shown in Fig. 1 are combinations of monolayer adsorption and capillary condensation, it has long been customary to estimate the pore size distribution of catalysts by using the Kelvin equation

$$r = \frac{-2\sigma V \cos \theta}{RT \cdot 2.3 \log p/p_0} \quad (15)$$

where σ is the surface tension of the liquid adsorbate at temperature T of the experiment, V is the molecular volume of the adsorbate, p/p_0 is the relative pressure, R the gas constant, and θ the angle of wetting of the adsorbate on the solid. The advent of the theory of multilayer adsorption and the establishment of the existence of such adsorption as a definite phenomenon has made pore size calculations of this simple type untenable and unreliable because part of the increased gas pickup is due to multilayer adsorption rather than to capillary condensation. However, within the last few years Wheeler (42), Ritter (43), and Shull (44) have proposed various methods for differentiating between the portion of an S-shaped isotherm due to multilayer adsorption and the portion that is to be attributed to capillary condensation. They have succeeded, therefore, in applying the Kelvin equation in such a way as to obtain estimates of pore size distribution in spite of the existence of multilayer adsorption.

The details of the procedures followed separately by these three authors have not all been published. They have, however, all been discussed at summer conferences of the A.A.A.S. on catalysis. It will suffice, therefore, merely to outline the general procedure used by these authors and to point out that their work is being submitted for publication in the very near future. Wheeler (42) set up an equation in which the total amount of adsorbate held by the catalysts at any given relative pressure was visualized as being made up of that portion held by multilayer adsorption and another portion held by capillary condensation. Furthermore, he modified the Kelvin equation slightly by postulating that the radius calculated by eq. (15) is not the radius of the empty pore but that of the hole left in the pore after the statistical number of layers predicted by the B.E.T. equation had been permitted to build up. Then by trying various Gaussian or Maxwellian distribution curves for the pores, he was able to deduce a pore distribution that would fit the adsorption data when both multilayer adsorption and capillary condensation were taken into consideration. Shull (44) carried out a similar treatment except that instead of using the B.E.T. equation to represent adsorption at high relative pressures, he estimated the multilayer

adsorption from a composite curve for nitrogen isotherms on a number of nonporous solids. He also improved the mathematical technique for deducing the pore distributions that will fit experimental isotherms of unusual shape. The approach of Wheeler and Shull to the problem is indirect in the sense that it merely confirms the agreement between the adsorption isotherms and certain pore distributions without showing necessarily that the distributions arrived at are the only ones that will give the observed

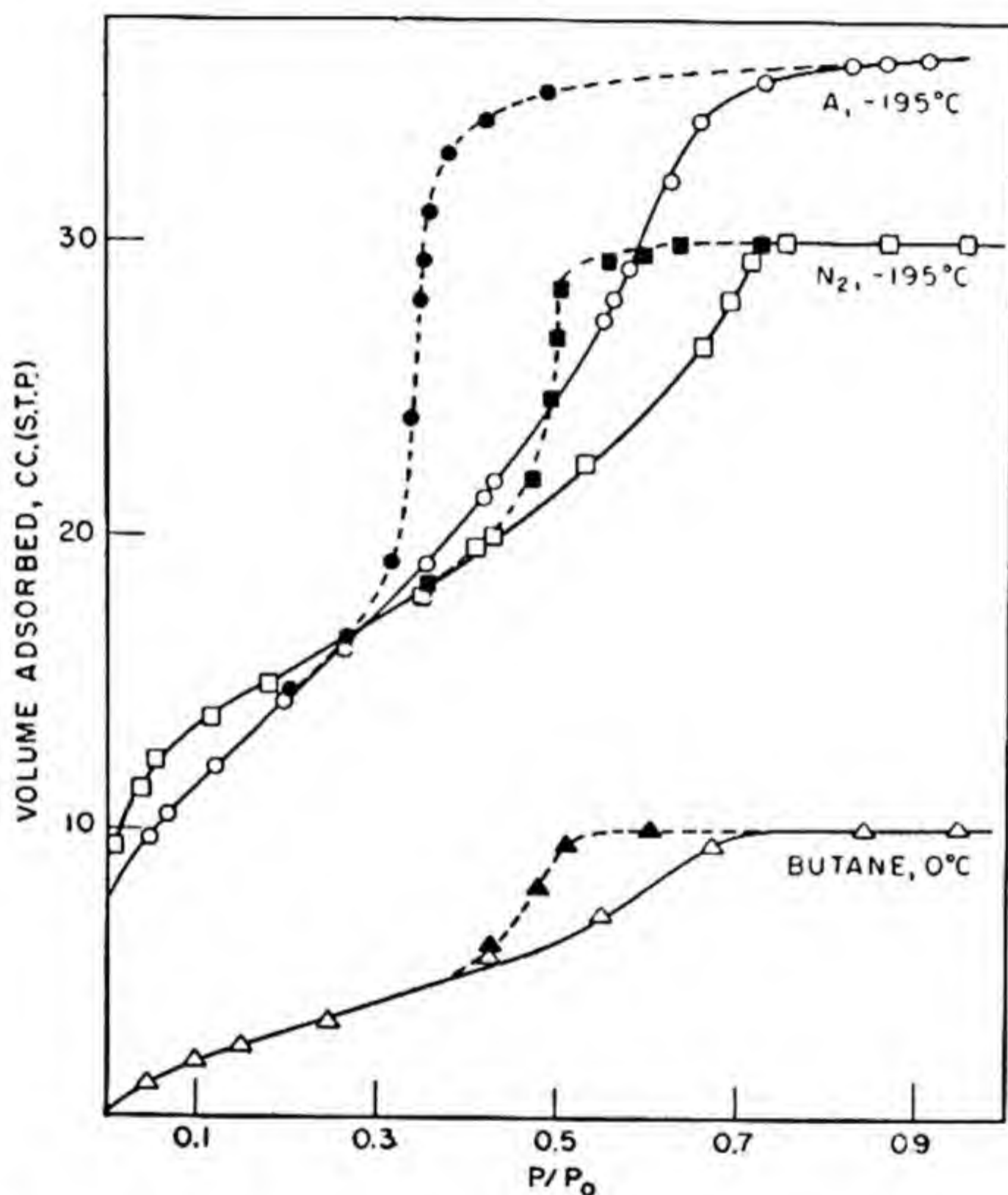


FIG. 8. Adsorption isotherms for argon, nitrogen, and butane on porous glass No. 3. Open symbols, adsorption; closed symbols, desorption (45b).

form of adsorption and desorption isotherms. Actually, these pore calculations are usually applied to desorption rather than to adsorption isotherms since it is generally believed that capillary condensation is more accurately measured by the Kelvin equation on desorption than on adsorption.

b. Pore Size from Pore Volume and Surface Area. A less elaborate but frequently used method for estimating the average size of the pores of a

solid makes direct use of surface area measurements. It is well known (Emmett and De Witt, 45a) that an estimate of the average pore size of a series of cylindrical capillaries can be obtained from the equation

$$\text{Radius} = \frac{2V}{A} \quad (16)$$

where V is the pore volume in cubic centimeters and A is the area of the porous adsorbent in square centimeters. As an illustration of this method reference may be made to the curves in Fig. 8 for the adsorption of nitrogen, argon, and butane on a sample of porous glass (Emmett and Cines, 45b).

If the pore volume is calculated from the saturation adsorption value of each isotherm and the surface area is measured by the nitrogen adsorption isotherms in conjunction with eq. (8), one obtains average pore radii of 16.7, 15.6, and 15.5 Å. from the nitrogen, argon, and butane curves respectively of Fig. 8. These radii are in very good agreement with the one obtained (17.7 Å.) by applying eq. (15) directly to the nitrogen desorption isotherm and assuming that the radius calculated by eq. (15) is the size of the hole left after the capillary walls are covered with a single layer of adsorbed molecules.

6. *Sintering Studies*

Finally, the surface area measurement method has proved to be very useful in following the changes in catalysts during use, during sintering, and during impregnation with promoters or additional catalytic components. Ries (46) and his coworkers have been especially active in exploring this application. As a matter of fact, the multilayer adsorption method was originally developed in the hope of being able to trace the relation between the change on sintering in the activity of an iron synthetic ammonia catalyst as compared to the change in surface area.

7. *Present Status of the B.E.T. Method*

These few applications of surface area measurements of catalysts certainly do not exhaust the list of possible applications but they help to illustrate some of the principal ways in which such areas can prove useful in a study of solid catalysts. They will doubtlessly be supplemented by many more examples as a larger number of workers begins to take advantage of the adsorption methods for following the surface areas and pore distributions of their catalytic materials.

The author prefers to consider the B.E.T. and other methods for measuring surface areas by physical adsorption isotherms as still in the process of change and development. New suggestions, modifications and improvements in the method are to be expected. Nevertheless the measurement of catalyst areas by gas adsorption methods may be considered even

now to rest on a very solid foundation and may be used with confidence as a tool in helping to elucidate the factors that influence the activity of catalysts.

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The Geometrical Factor in Catalysis

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The Gas Light and Coke Company, London

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I. INTRODUCTION

Many years before reliable information was available concerning the actual structure of any catalyst, attempts were made to consider the disposition of a reacting molecule on the active surface. So long as these conjectures were confined to reactants which were adsorbed by single atoms of the catalyst surface, little progress could be made by such hypotheses. Burk (1), however, studied the implications of two-point adsorption of diatomic molecules and came to the conclusion that some of the known facts concerning catalyst poisons could be accounted for by the assumption that this mechanism was involved.

Balandin (2) shortly afterwards began the publication of a series of papers developed from the theory that the catalytic decomposition of a relatively large molecule could only take place by simultaneous adsorption at several points; this was known as the Multiplet Theory. With cyclohexane, for example, attachment at six centers was supposed to be necessary before benzene could be formed by the loss of three hydrogen molecules. Calculations along these lines for metallic catalysts, whose lattice dimen-

sions were known, indicated that the distances involved were of the same order of magnitude as those of the C—C distances in benzene.

Although the original form of this theory has been seriously criticized for several reasons (3), it provided a stimulus to further interest in problems of this type. Subsequent study of the relation between the dimensions of organic molecules, and of the catalysts which are effective in their conversions, has proved most interesting and has established the fact that two-point adsorption frequently occurs. It is with reactions of this type that this article is concerned; in particular, the importance of the geometrical factor in defining the properties of a catalytic surface is considered.

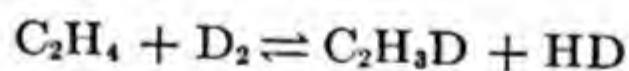
The reactions to which attention will be given are confined to a relatively narrow range, although others are likely to be found in due course which are suitable for similar treatment.

II. REACTIONS OF UNSATURATED ORGANIC MOLECULES

1. Ethylene and Olefins

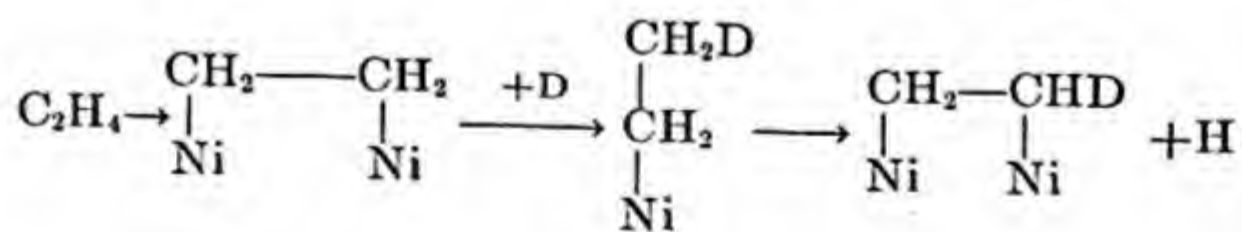
The classical researches of Sabatier and his colleagues revealed the wide applicability of metallic nickel as a catalyst for the hydrogenation of the olefinic double bond. Many years passed before the mechanism of this type of conversion was disclosed; this resulted from the discovery of deuterium, which made possible a study of the exchange reactions of ethylene. Because of its important bearing on geometrical problems, a brief account of this work must be included.

When deuterium and ethylene are brought together in contact with a nickel catalyst, the exchange reaction



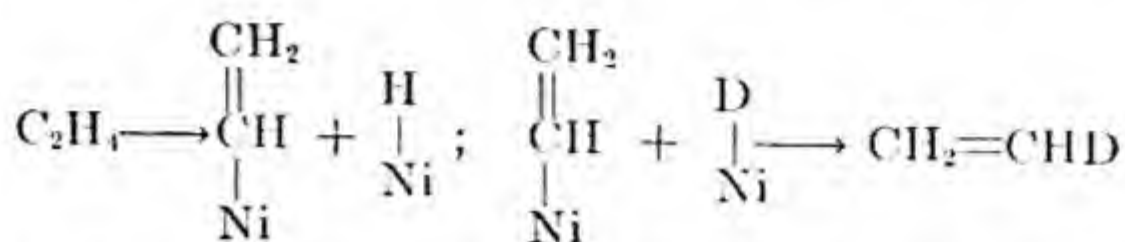
takes place. Two explanations of the mechanism of this exchange can be suggested, represented by the following series of changes.

a. The associative mechanism, as proposed by Horiuchi and Polanyi (4),



in which the ethylene molecule is adsorbed on two adjacent nickel atoms by opening of the double bond, then reacts with an adsorbed deuterium atom to give a product adsorbed at one point only, but, by loss of a hydrogen atom, reverts to an adsorbed ethylene molecule containing D.

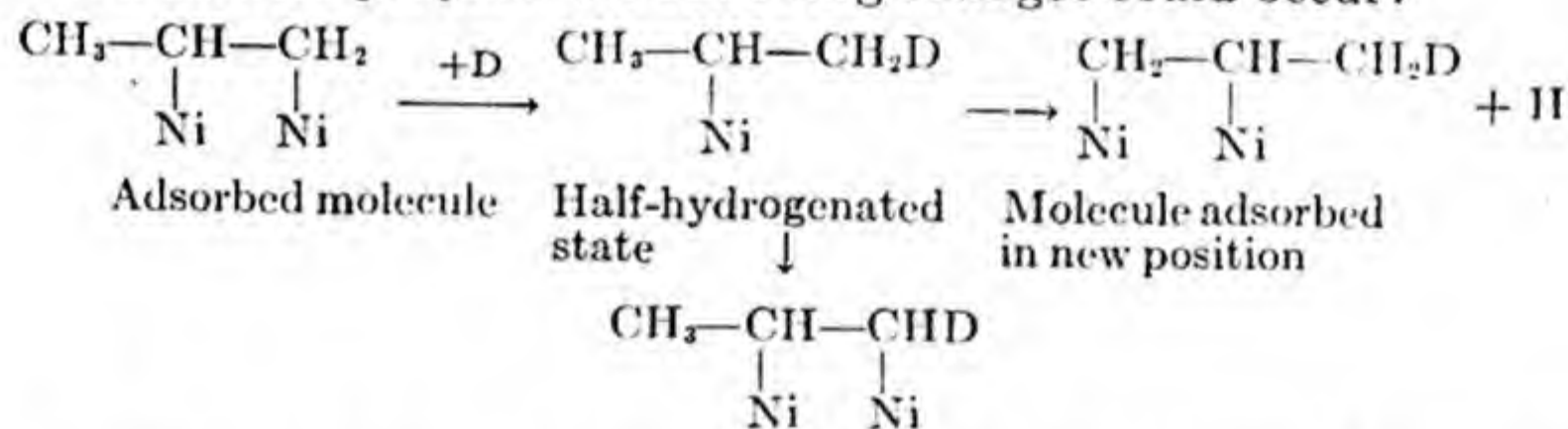
b. The dissociative mechanism due to A. and L. Farkas (5)



in which single point attachment to the catalyst is involved.

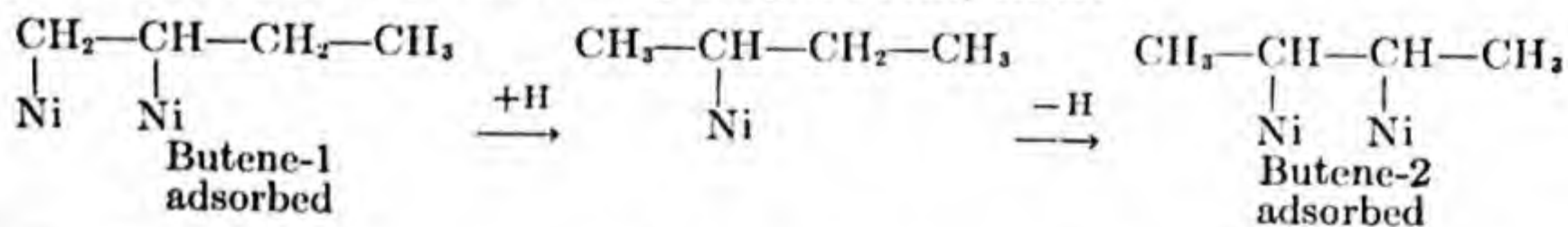
After many conflicting statements concerning these alternatives, the correctness of the associative mechanism was established by the work of Conn and Twigg (6a and b) which showed that no exchange takes place between C_2H_4 and C_2D_4 under conditions in which exchange between C_2H_4 and D_2 occurs. This proved that no free hydrogen or deuterium atoms were formed from the hydrocarbon alone. This conclusion was confirmed by further experiments with olefins of higher molecular weight. These revealed two very important facts: (1) that all the hydrogen atoms in the higher olefins, not only those adjoining the double bond, are capable of exchange with deuterium, and (2) that double bond migration can accompany the exchange reaction but only in the presence of hydrogen.

These results would be expected from two-point adsorption of the olefin. Thus, with propene the following changes could occur:



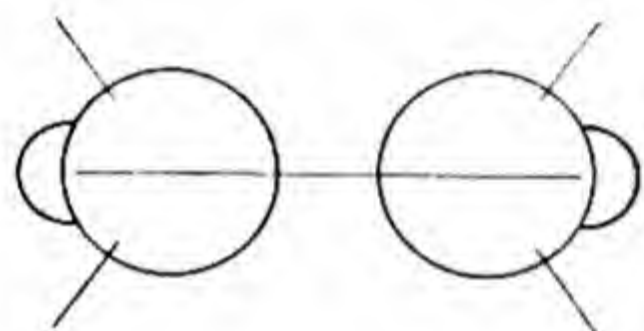
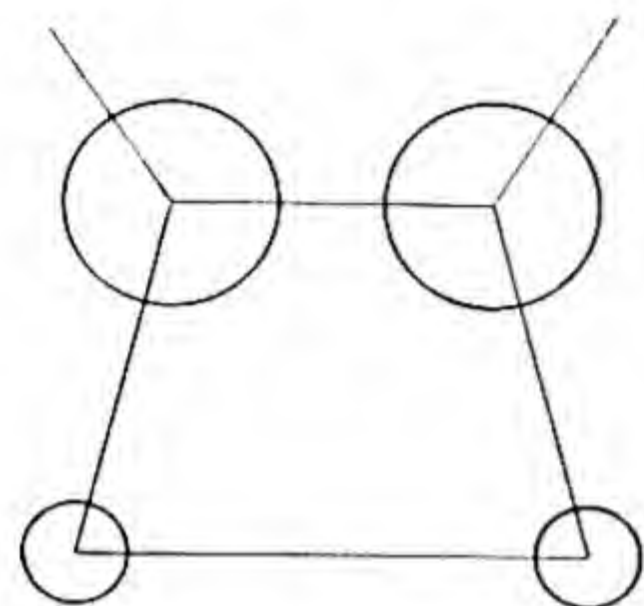
so that the desorbed molecule may be $\text{CH}_3\cdot\text{CH}=\text{CHD}$ or $\text{CH}_2\text{D}\cdot\text{CH}=\text{CH}_2$.

With butene, again, migration of the double bond could take place by successive addition and loss of a hydrogen atom, thus:



Following these experimental investigations, Twigg and Rideal (7) considered the actual disposition of ethylene on the nickel lattice. This consists of a face-centered cube having a side of 3.50 Å., in which the closest Ni-Ni distance is 2.47 Å. If the C-C distance in ethylene is taken as 1.54 Å. and the Ni-C distance is assumed to be 1.82 Å., the same as in nickel carbonyl, then the adsorbed ethylene molecule will fit on the close Ni-Ni spacing as shown in plan and elevation in Fig. 1, with a slight distortion of the Ni-C-C angle from the normal value of $109^\circ 28'$ for the tetrahedral bond. It will not fit on the wider nickel spacing of 3.50 Å. (Slightly differ-

ent results will be obtained in this and similar calculations if the interatomic distances between metal and carbon are derived from the sum of the covalent radii for the respective atoms, this method giving a longer carbon-metal bond.) It is, therefore, evident that two-point adsorption of ethylene



1 Å

FIG. 1. The ethylene molecule adsorbed on nickel. The large circles represent carbon atoms, the small circles nickel atoms. Bond lengths and angles are to scale, but not circle diameters.

ethylene under conditions where much of it still remained bare in the presence of trimethylethylene.

From the discussion above, it may be concluded that for reactions requiring two-point adsorption there should be a direct relation between the number of pairs of atoms in the catalyst surface at the correct spacing, and the catalytic activity. Confirmation of this effect has been provided by the work of Beeck, Smith, and Wheeler (9) on the hydrogenation of ethylene. As catalysts, they used films of nickel deposited by evaporation

might occur, with slight distortion of the bond angles or some small displacement of the metal atoms from their normal lattice, on metal catalysts where the spacing is between about 2.4 Å. and 2.8 Å. In this group nickel, cobalt, copper, platinum, and palladium can be found and all of them can be used for the hydrogenation of olefinic double bonds.

When a high concentration of olefin molecules is present, steric effects must also be considered. For example, the closest possible packing of ethylene molecules on the 110-plane of nickel, results in no interference between adjacent molecules, and the whole surface should be nearly covered by the hydrocarbon. This is in accordance with the fact that ethylene can completely retard the conversion of para- to ortho-hydrogen on a platinum catalyst under conditions of relatively low temperature or high ethylene pressure (Farkas, Farkas, and Rideal, 8). With methylethylenes, interference between adjacent molecules becomes evident because of the large space occupied by the $-\text{CH}_3$ groups. The reality of this steric effect has been demonstrated by Twigg and Rideal (7) using the reaction $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ as a means of evaluating the amount of uncovered catalyst surface. They observed that a given catalyst could be completely covered by

onto glass under conditions where layers some 200-atoms thick were still fully accessible to the reactants. When the catalyst was prepared in a vacuum, the film was not oriented, but when nitrogen was present, the layer was completely oriented to expose the 110-plane in which the desired spacing occurs, and its catalytic activity per unit of surface was five times as great. Examination of this type of catalyst by electron diffraction methods by the above investigators has contributed valuable additional evidence in support of the postulate of the geometrical relationships between reactant and catalyst.

2. *The Hydrogenation of Other Unsaturated Organic Molecules*

Much of what has been said above can be applied to other hydrogenation reactions where the saturation of a double bond is involved. With many of these substances the steric factor must also be important, as the two-point attachment must often take place at or near the center of a long chain. With some reactions of this type it is probable that a departure from the normal nickel lattice may give increased activity, for it has already been noted that the 2.47 Å. spacing on nickel is not quite ideal; this applies still more if the C-Ni distance amounts to 2.0 Å. rather than to the lower value of 1.82 Å. derived from nickel carbonyl.

Evidence has recently been provided by the work of de Lange and Visser (10) on nickel catalysts deposited on kieselguhr. This has established that the normal lattice of metallic nickel does not occur in materials prepared in this way, and that the reduced active catalyst is obtained as a result of the attack of hydrogen on a nickel hydrosilicate. By interaction of the diatomite and the nickel hydroxide deposited on it, an entirely new lattice is produced which provides a greatly increased total surface of catalyst, and which leads in the finished state to a widely dispersed and very stable arrangement of nickel atoms. It will be of great interest to obtain further evidence as to the exact distance between pairs of nickel atoms in this catalyst, which is of exceptionally high activity.

III. REACTIONS OF ACETYLENE

The reaction between acetylene and hydrogen, in contact with metallic catalysts, not only results in the formation of ethylene and ethane but also of products with much higher molecular weights. This latter process occurs at temperatures well below those required for the polymerization of acetylene alone, in the presence of the same metals. Sheridan (11) has studied the kinetics of the reactions involved and has thereby contributed to the understanding of the geometrical conditions which exist on such catalysts. Although the total disappearance of acetylene was largely

independent of temperature in the range 0–130°, the proportions of ethane, ethylene, or heavier hydrocarbons varied, the simpler hydrogenation reactions having lower apparent activation energies. These differences between the behavior of ethylene and acetylene, on hydrogenation with simple metallic catalysts, probably arises from the greater unsaturation of acetylene. The adsorbed ethylene molecule, held at two points, probably has the carbon-carbon skeleton of ethane; acetylene similarly held has that of ethylene and the C≡C distance is therefore 1.33 Å. instead of 1.54 Å. for C—C. The half-hydrogenated state for acetylene therefore has the structure CH=CH₂ or —CH—CH₂. In the latter, one of the carbon



atoms has an unpaired electron which could lead to its taking part in a polymerization reaction. Sheridan has considered all three possible processes from the geometrical viewpoint.

Assuming the C—Ni distance to be 2.0 Å., the C—Pd distance to be 2.1 Å., the C—Pt distance to be 2.1 Å., and the angle M—C=C to be 121°, the required spacings for two-point adsorption of acetylene become 3.33 Å. for nickel, and 3.43 Å. on palladium or platinum; the spacings for ethylene adsorption would similarly be 2.87 and 2.94 Å. Those actually available are 2.48 and 3.5 Å. for nickel, 2.75 and 3.88 Å. for palladium and 2.75 and 3.91 Å. for platinum. Some strain, therefore, is required to fit ethylene to any of these lattices, and in an opposite direction to fit acetylene on the long spacing. On purely geometrical grounds, the adsorption of ethylene on the more abundant short spacing might be expected to outweigh that of acetylene; in fact, however, acetylene is more strongly adsorbed, and it is evident that additional factors must be involved.

The hydrogenation of acetylene may therefore be explained by a mechanism very similar to that already discussed for ethylene, and of course the two reactions can go forward simultaneously on the different spacings of the same catalyst. The formation of higher hydrocarbons can also be explained by similar postulates, as follows. The characteristic feature of the adsorbed acetylene molecule is that it is still unsaturated, whereas adsorbed ethylene is not. Moreover, it is important to note that the polymerization reaction with acetylene takes place when hydrogen is present but does not occur in its absence; it therefore seems likely that the half-hydrogenated state of acetylene plays a vital part in the process.

For ethylene, the corresponding intermediate is CH₂—CH₃, but for

acetylene it must be either CH=CH₂ or —CH—CH₂. In the latter, there

$$\begin{array}{ccc} | & & | \\ \text{Ni} & & \text{Ni} \end{array}$$

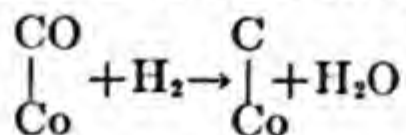
is a carbon atom with an unpaired electron which may take part in a chain reaction with other adsorbed acetylene molecules and produce hydrocarbons of various molecular weights, due to the presence of molecules in the half-hydrogenated state. The disposition of the polymer on the nickel catalyst is different from that required for the initial acetylene adsorption, and the process may be expected to continue when both the long and short Ni—Ni spacings are available, as they are on the 110-plane of nickel. Whether the building up of the polymer requires simultaneous adsorption of several carbon atoms or not is uncertain, but this particular matter is not of primary importance. It does, however, appear to be most probable that the half-hydrogenated acetylene fragment held on the 2.47 Å. pair of nickel atoms will react with the terminal pair of a larger olefin molecule held on an adjacent pair of the same spacing, and there is no need to suppose that the whole of the larger chain is held. This view is supported by the fact that the branched paraffins which are formed contain only single methyl groups in the side chains. It is not justifiable to carry these conjectures any further without much more experimental evidence, but the results thus far available indicate that adsorbed ethylene has the ethane skeleton while adsorbed acetylene has the ethylene skeleton, and that the differences in their behavior can be explained on this basis.

IV. THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE, AND RELATED REACTIONS

1. *The Fischer-Tropsch Process*

Metallic catalysts of the iron-cobalt-nickel group again come under consideration when evidence is brought forward as to the geometrical requirements of the Fischer-Tropsch synthesis. Although many features of this process have no direct bearing on the geometrical study of the catalysts which are used, it is necessary to give a brief summary of their salient points in order to present all the evidence in proper perspective. The work of Craxford (12) and of Herington (13) has shown that when carbon monoxide and hydrogen are passed over catalysts consisting essentially of metallic cobalt, a series of reactions takes place which may be represented by the following scheme:

a. Carbon monoxide is adsorbed by the metal, and in this state reacts with hydrogen, producing water and a surface layer of cobalt carbide.



b. More hydrogen then reacts with the carbide to form adsorbed —CH₂— groups held by the surface cobalt atoms. If the conditions are

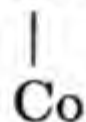
such that there are numerous adsorbed hydrogen atoms also present, then these $\text{—CH}_2\text{—}$ groups will be converted into methane and no synthesis of higher aliphatic hydrocarbons will take place. More favorable results, however, arise when relatively few hydrogen atoms are adsorbed, and when the catalyst surface is almost completely covered by hydrocarbon fragments or carbide.

c. Under these conditions, two adjacent —CH_2 fragments combine to

$$\begin{array}{c} | \\ \text{Co} \end{array}$$

produce adsorbed ethylene held on two adjacent cobalt atoms.

d. Growth of the hydrocarbon chain then occurs by reaction of a further adsorbed $\text{—CH}_2\text{—}$ fragment with the ethylene molecule, in a manner similar to that involved when deuterium exchanges with ethylene, and to that suggested for the production of higher hydrocarbons from acetylene. Intermediates of the type $\text{CH}_2\text{—CH=CH}_2$ can be readsorbed



on two Co atoms, by migration of hydrogen, in the form $\text{CH}_2\text{—CH—CH}_3$.

$$\begin{array}{cc} | & | \\ \text{Co} & \text{Co} \end{array}$$

e. This process can be repeated, the double bond generally migrating to the terminal pair of carbon atoms so that the hydrocarbon formed usually has a straight chain. The chances of reaction of a $\text{—CH}_2\text{—}$ fragment with a larger molecule held by a pair of carbon atoms other than those at the end of the chain are less likely, but this process will sometimes take place and will give rise to an isomer in which the branch consists of a single methyl group. Equal growth of two branches to any considerable length is unlikely to occur on steric grounds.

f. Desorption of the hydrocarbon will thus produce a 1,2 olefin, or, following hydrogenation of the double bond, a paraffin.

g. Cracking of large hydrocarbons, sometimes accompanied by hydrogenation, may also take place on the same catalysts.

Apart from the conclusions derived from a study of the direct synthesis, certain other factors support the correctness of this picture of the geometrical relations between catalyst and reactants. If the interatomic distance and bond angles were not important in controlling the synthesis, it might be supposed that the adsorbed $\text{—CH}_2\text{—}$ fragments all link together into a few giant molecules covering nearly the whole surface, and that hydrocarbons of varying molecular weight are then produced by splitting of the macromolecules.

But such a picture would imply that most of the C—C and the C—Co bond angles were 90° , would leave no room for the attachment of hydrogen

atoms, and would be expected to produce many types of branched-chain hydrocarbons.

To reject such a picture does not mean that large aliphatic hydrocarbon molecules cannot cover a great deal of the surface. As an example, Fig. 2 shows at A the projection of a C_{15} chain which is adsorbed by two

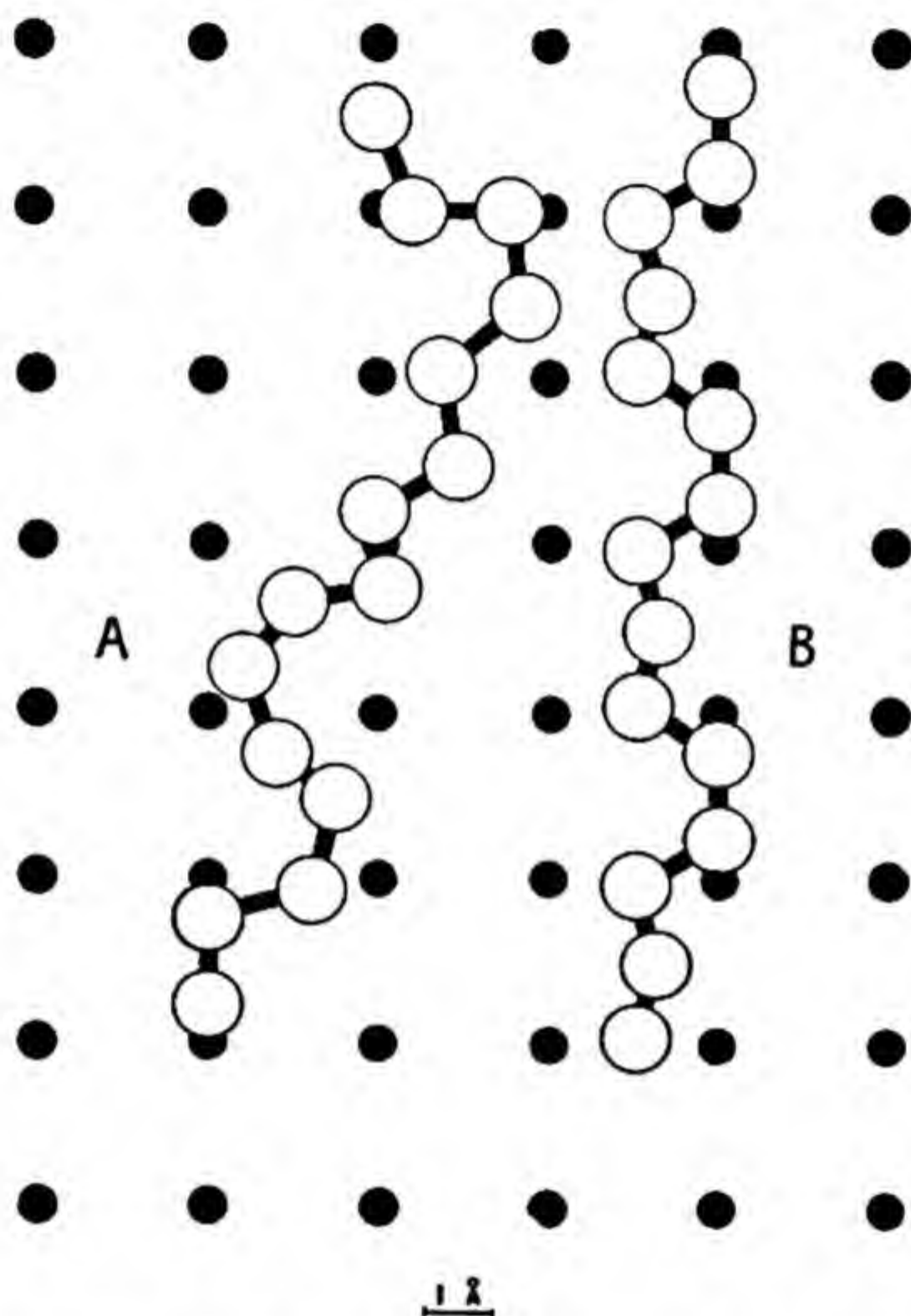


FIG. 2. The disposition of a C_{15} chain on a metallic cobalt catalyst.

A — attachment by two distant pairs of carbon atoms, with little departure from the planar zigzag chain.

B — attachment to six cobalt atoms in one row, with extensive departure from the planar chain.

Cobalt atoms shown as full black circles.

pairs of carbon atoms on two pairs of cobalt atoms in a 100-plane of the metal catalyst. Some departure from the planar form of hydrocarbon chain is necessary to give this arrangement, but the normal bond angles can be retained. Such an attachment effectively blocks much of the surface, and several similar molecules could pack closely side by side. In actual practice, Fischer catalysts are well known to suffer from gradual

deterioration by the building up of waxy hydrocarbons, which are not normally desorbed but which can be removed from the surface by treatment with hydrogen. The mechanism of this cleaning process is apparent from the diagrams of Fig. 2, as the attack of hydrogen atoms can take place in a system like this and will result in desorption of the hydrocarbon. It is even possible to imagine a long-chain paraffin molecule adsorbed at many points so that every cobalt atom in a row is occupied, as in B of Fig. 2. This arrangement requires repeated C_5 units to fit in place. The chances of such an arrangement are much smaller than those of adsorption as shown in Fig. 2 (A) where so many more centers are available. Similar arguments apply to the 110-plane of a cobalt or nickel catalyst, in which the atoms are arranged in parallel rows, with a row to row distance of 3.5 Å. and an internal row spacing of 2.5 Å.

One further piece of evidence can be brought forward supporting the chain growth hypothesis. Since adsorbed ethylene is present, according to this view, it should be possible to incorporate this hydrocarbon into the larger molecules built up in the synthesis, by adding it to the reacting mixture of carbon monoxide and hydrogen. That this can be done was demonstrated at an early date by Smith, Hawk, and Golden (14). On the other hand, acetylene added to the gas should not take part in the synthesis, as it can only be adsorbed on the wider spacing of cobalt or nickel atoms, and enough hydrogen to convert it to ethylene is extremely unlikely to be present in the adsorbed state on adjoining metal atoms. Herington (13) has shown that this prediction is correct and that acetylene is not converted into higher boiling products during the synthesis.

2. *Other Syntheses Related to the Fischer-Tropsch Process*

Comparatively little is yet known of some synthetic reactions which obviously resemble the Fischer-Tropsch process very closely, but they are worth brief mention because they are also likely to be controlled by geometrical factors. The Oxo synthesis (15) of aldehydes by the interaction of ethylene or other olefins with carbon monoxide and hydrogen is carried out in contact with cobalt catalysts at temperatures in the range 110–150°, and under a pressure of 100–200 atmospheres. Cyclic olefins react similarly; for example, cyclohexene gives hexahydrobenzaldehyde. There can be little doubt that a two-point adsorption of the hydrocarbon must take place and that the adsorbed molecule then reacts with carbon monoxide and hydrogen; the difference between this process and that responsible for the normal hydrocarbon synthesis is that adsorbed carbon monoxide survives as such under the less drastic temperature conditions which are employed. Owing to the fact that a variety of isomeric aldehydes are produced, this system deserves further detailed study on geometrical lines.

A modified type of hydrocarbon synthesis, known as the "Iso-synthesis," also requires much more attention because the catalysts here employed are oxides and not free metals (16). Mixtures of thoria, alumina, and zinc oxide are used at about 450° under high pressure, and produce good yields of 2-methylpropane; at higher temperatures naphthenes and aromatic hydrocarbons also appear, while at lower temperatures isobutyl alcohol can be isolated. By passing dimethyl ether and hydrogen over the catalysts, hydrocarbon products are obtained similar to those from CO and H_2 . The ether is therefore likely to be an intermediate. More will be said about the structure of oxide catalysts in the following sections.

V. THE FORMATION OF AROMATIC FROM ALIPHATIC HYDROCARBONS

In comparison with the information about geometrical factors for metallic catalysts, little parallel progress has been made with oxides or sulfides. This is largely due to the uncertainty which exists concerning the precise chemical composition of these catalysts in their active state, and partly to the lack of reliable data for the crystal structures of some of the lower oxides and sulfides.

However, there are one or two instances where enough is known about catalysts of these types to justify some attention at this point. Some of the most thoroughly investigated cases constitute the group of catalysts used in the ring-closing reactions which lead to the production of aromatic hydrocarbons from paraffins or olefins. These consist of oxides of vanadium, chromium, and molybdenum, or of complex and supported catalysts containing one of these oxides.

Herington and Rideal (17) have studied a series of catalysts containing molybdenum, which were prepared by the reduction of MoO_3 , of supported MoO_3 , and of complex molybdates. These had activities ranging from zero for the plain oxide to high values for some of the complexes and for MoO_3 supported by alumina. It was found that the plain oxide could be reduced at temperatures above 500° , while the supported catalyst remained in the form of oxide; similar differences were disclosed among the complex molybdates. Ammonium cupromolybdate, for example, was reduced to metallic molybdenum and was inert, while other compounds, such as vanadomolybdates, although they decomposed, led to catalysts in which MoO_2 persisted.

These facts suggested that the oxide MoO_2 was essential in bringing about the ring-closing reaction, and the special features of its crystal lattice were considered. This is of the rutile type (body-centered tetragonal system) and is shown in Fig. 3, together with a plan of the 110-plane in Fig. 4. Here the shortest distance between molybdenum atoms is 2.79 Å., the next

closest spacing being 3.71 Å. For a two-point adsorption of an olefin on adjacent molybdenum atoms at 2.79 Å., the Mo—C—C angle works out at 108° instead of the tetrahedral angle; only slight distortion is therefore necessary. Molybdenum metal, on the other hand, is a body-centered cubic crystal with an edge of 3.14 Å. and the shortest Mo—Mo distance 2.2 Å.; two-point adsorption on this lattice was considered less likely than on the oxide. In view, however, of what is said later about the properties of molybdenum disulfide, it does not appear that this explanation of the inactivity of the

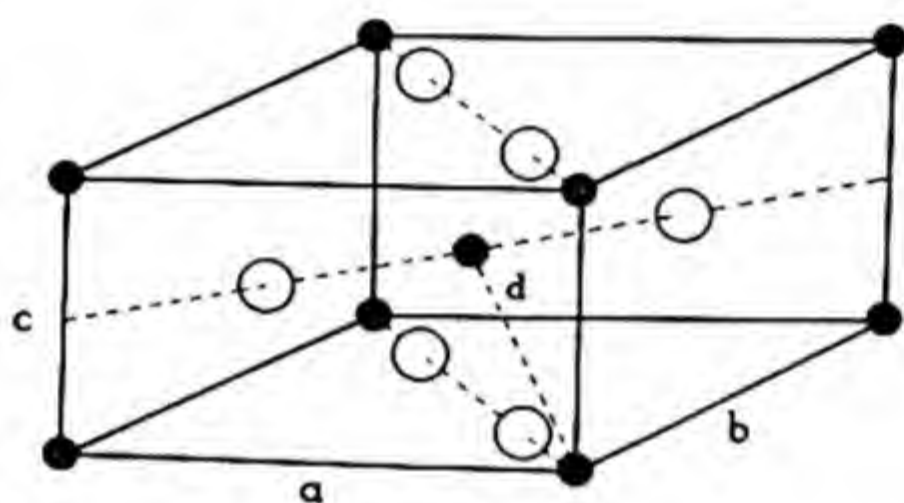


FIG. 3. The unit cell of MoO_3
Molybdenum atoms, full black circles
Oxygen atoms, open circles

$a = 4.86 \text{ Å.}$
 $b = 4.86 \text{ Å.}$
 $c = 2.79 \text{ Å.}$
 $d = 3.71 \text{ Å.}$

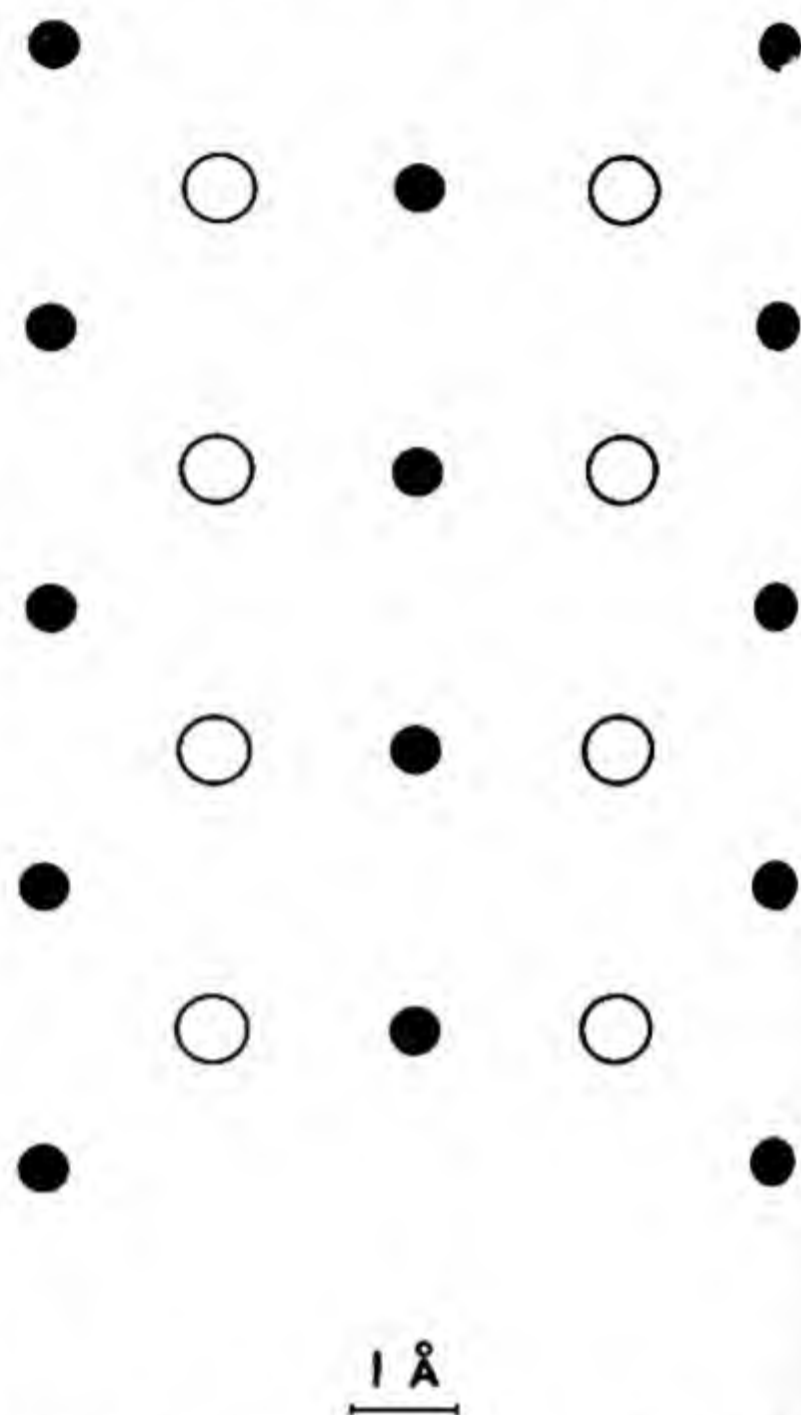


FIG. 4. Plan of the 110-plane of MoO_3 .
Molybdenum atoms, full black circles
Oxygen atoms, open circles

metal is satisfactory, and some other reason must exist. It may, for example, be due to the absence of oxygen atoms, or to a drastic shrinkage of the surface of the catalyst on conversion of the oxide to the metal.

Some other features of these ring-closing catalysts are also interesting from the geometrical aspect. If it is assumed that the formation of an aromatic hydrocarbon can only occur when the terminal pair of carbon atoms in a chain is adsorbed, then it is possible to calculate the probability for the conversion of various initial aliphatic hydrocarbons into aromatics; these probabilities are proportional to the rates of conversion under a given set of conditions. The results of such calculations (17) show excellent agreement with experimental figures, and this agreement between the two is strong evidence in support of the argument about the importance of the spacing on the catalyst surface.

Besides molybdenum oxide, chromium oxide catalysts are very important for the production of aromatics from open-chain hydrocarbons. Certain features of this series of catalysts still remain obscure, but it is already highly probable that their behavior may be explained on geometrical grounds. The important facts about these chromium oxide catalysts are as follows: Cr_2O_3 gel, prepared by precipitation of chromic salts by ammonia, yields a highly active catalyst on treatment with hydrogen. This activity is not retained on prolonged use, and falls off rapidly when the material is regenerated by oxidation; this decay is due to conversion to crystalline Cr_2O_3 (Visser, 18) which has been shown to be inactive (Turkevich, Fehrer, and Taylor, 19).

But if the chromium oxide is deposited on alumina, it retains its original high activity and even survives regeneration by oxidation at quite high temperatures. Moreover, the pretreatment of the alumina makes an appreciable difference to the activity of the catalyst, although Al_2O_3 itself is quite inert as a catalyst for the ring-closing reaction. Figure 5 shows the

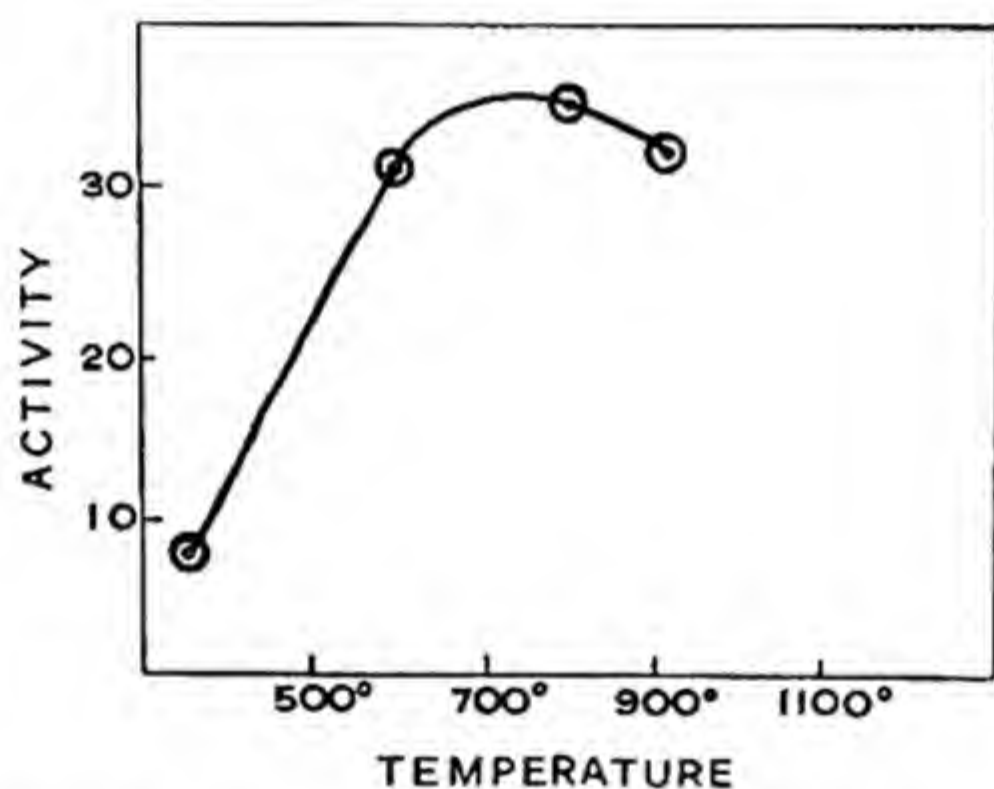


FIG. 5. The activity of chromium-oxide-alumina catalysts for production of aromatic hydrocarbons. Effect of temperature to which $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ has been heated before application of CrO_3 .

activity of chromium oxide-alumina catalysts in relation to the temperature to which the hydrated alumina has been heated before deposition of the chromium oxide (Griffith and Morcom, 20). In Fig. 6 is shown the effect of temperature on the conversion of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$, these results being due to Biltz (21). These together provide strong evidence that the alumina is most effective in the anhydrous γ -form. It is, therefore, very likely that the active chromium oxide catalyst exists in the form of $\gamma\text{-Cr}_2\text{O}_3$, with a crystal lattice closely resembling that of $\gamma\text{-Fe}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$, but not capable of existence by itself under the conditions of the catalytic conversion.

Visser (18) has attempted to identify this form by X-ray examination, but has not been successful; he has, however, shown that a pure Cr_2O_3 catalyst heated at 475° for 1 hour has a surface area of $28 \text{ m}^2/\text{g}$., while a preparation containing 30% Al_2O_3 had a surface of $168 \text{ m}^2/\text{g}$. In view of these observations it is also very likely that ring-closing catalysts obtained by depositing

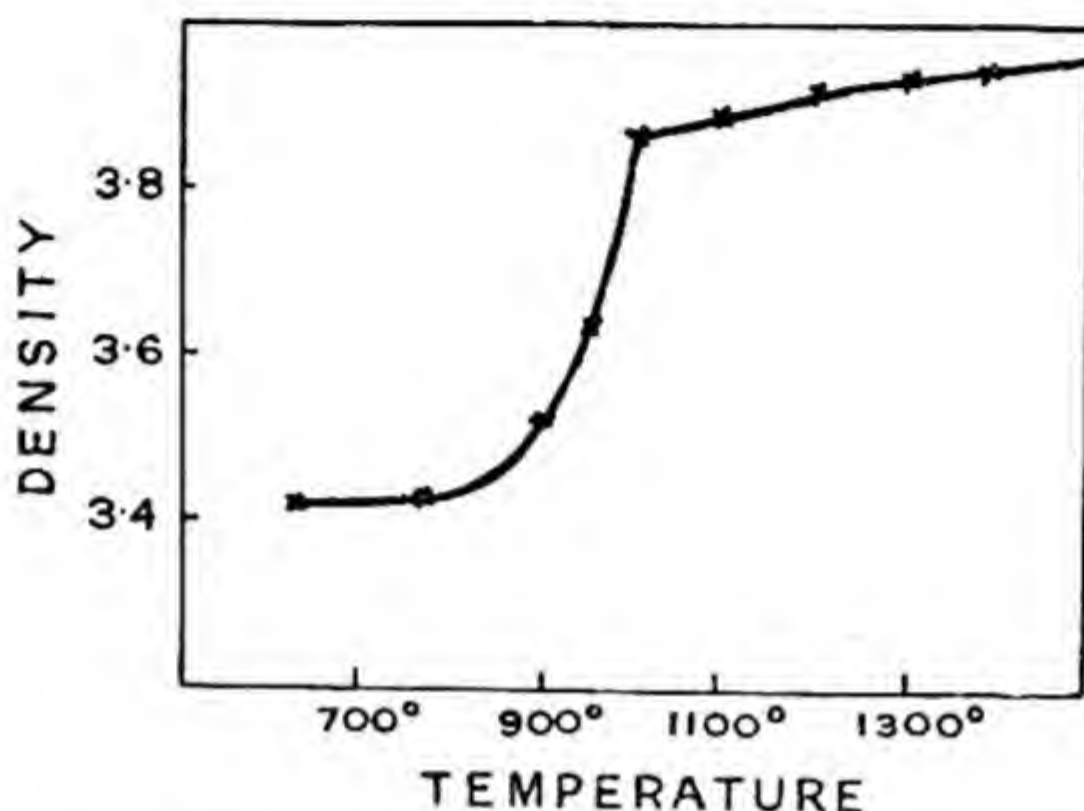


FIG. 6. The conversion of $\gamma\text{-Al}_2\text{O}_3$ into $\alpha\text{-Al}_2\text{O}_3$. The transition temperature coincides with the point in Fig. 5 where activity declines after passing the maximum.

MoO_3 and V_2O_5 on alumina, the latter being described by Kazansky *et al.* (22), also function in a crystalline form isomorphous with $\gamma\text{-Al}_2\text{O}_3$.

The lattice of $\gamma\text{-Al}_2\text{O}_3$ or $\gamma\text{-Fe}_2\text{O}_3$ is of the spinel type; Fig. 7 shows a plan of the 100-plane for a crystal of this series; a similar arrangement exists in several other planes. Some vacant metal atom spaces occur at unknown positions. It is evident that the metal atoms are here present in rows, and that the spacing is suitable for two-point adsorption of a hydrocarbon chain. Moreover, the wide spacing between parallel rows of metal atoms and the presence of two intermediate rows of oxygen atoms would be expected to diminish the tendency for other reactions to take place, and little choice is left to the adsorbed hydrocarbon chain except to form a ring. The conditions are not quite so severely limited in other planes of the crystal, and, in fact, all these catalysts suffer from side reactions which produce heavy polymers; the removal of these substances makes regeneration necessary. In the above argument, no attention has been given to the fact that hydrogen must be split off from the aliphatic hydrocarbon during its conversion. There is no evidence yet as to how this takes place, but it is possible that the oxygen atoms in the catalyst play some part in this process, and a mechanism like this would explain the inactivity of metallic molybdenum.

Ring closure with a sulfided catalyst has been described by Hummer and Taylor (23). When molybdenum dioxide supported on alumina was treated with sulfur compounds it was found to retain some of the sulfur and to gain in activity as a catalyst. It was, however, quite distinct in its properties from a normal MoS_2 catalyst which has a strong cracking action.

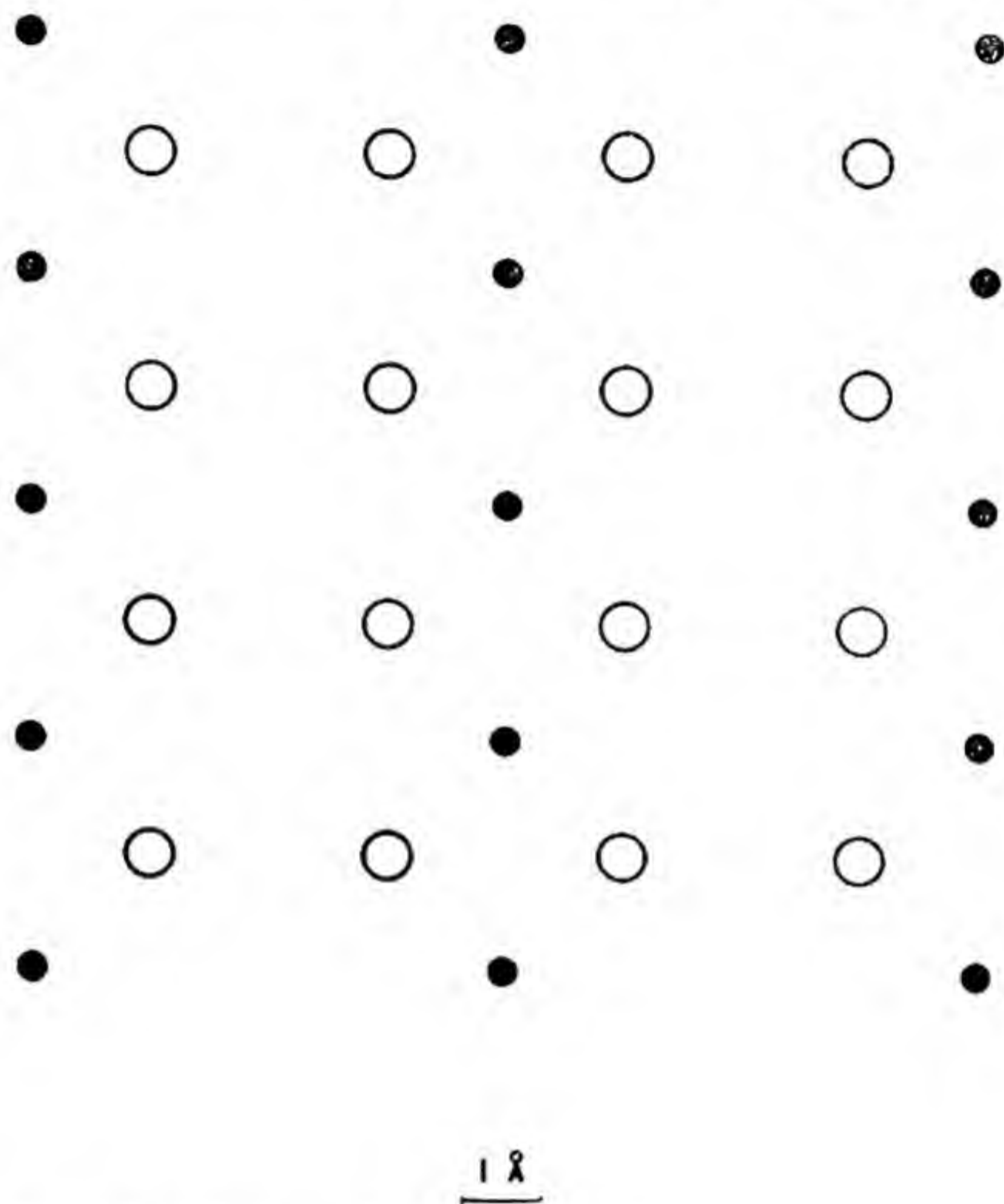


FIG. 7. Plan of the 100-plane of $\gamma\text{-Al}_2\text{O}_3$.
 Aluminum atoms, full black circles
 Oxygen atoms, open circles
 Dimensions for $\gamma\text{-Cr}_2\text{O}_3$ would be very similar. The lines of active atoms are widely separated.

It is therefore probable that the sulfided catalyst retains a spinel structure, in which partial replacement of oxygen by sulfur has occurred.

The fact that $\gamma\text{-Al}_2\text{O}_3$ itself is not a catalyst for ring closure is important, as it illustrates the great significance of the chemical character of the element concerned in determining the presence or absence of catalytic activity.

Herington and Rideal (24) have considered what products may be formed from a large variety of aliphatic hydrocarbons, on the assumption

that two-point adsorption always takes place but can often do so in more than one way. They have been able to give a satisfactory explanation of all the results which are obtained in practice with a catalyst consisting of chromium oxide on alumina, including those reactions which involve isomerization and the formation and rupture of secondary rings. The success of such approaches to the problems involved emphasizes the importance of studying thoroughly the structure of the catalysts used.

VI. THE DESTRUCTIVE HYDROGENATION OF HYDROCARBONS

A great many substances have been described as catalysts for the conversion of heavy hydrocarbons into those of lower boiling point, by treatment with hydrogen under pressure. Most of the publications on these processes are not concerned with the precise chemical composition of the catalysts but only with their rough classification into groups of the periodic system, so that it is not possible to gain much information from them which is useful for the present discussion.

There is, however, no doubt as to the exceptional activity of certain molybdenum compounds for this type of reaction; the disulfide is outstanding and the dioxide is also highly effective. What has already been said about the mechanism of ring closure on MoO_2 will have indicated that this oxide should be capable of adsorbing almost any olefin, and it could behave similarly towards those with a cyclic structure in suitable temperature ranges. The wide applicability of this catalyst is, therefore, no more surprising than that of metallic nickel for the hydrogenation of the olefinic double bond.

The molybdenum catalysts, unlike nickel, are not poisoned by sulfur compounds, and when such compounds are present in the hydrocarbon undergoing treatment, partial conversion of MoO_2 to MoS_2 will take place. For this reason, as well as because of the particularly high activity of the disulfide, it is of interest to consider the structure of MoS_2 with reference to the adsorption of organic molecules on its surface.

Molybdenum disulfide consists of a layer lattice with hexagonal symmetry.

Each plane of molybdenum atoms is held by covalent bonds between two planes of sulfur atoms; part of the structure is shown in Fig. 8. The important feature of this lattice is that the molybdenum atoms are arranged triangularly 3.15A. apart. Such planes could readily be exposed in a crystalline MoS_2 catalyst from which one layer of outer sulfur atoms had been removed by reaction with hydrogen. On this lattice, with the Mo—C bond 2.14A. it can be seen that two-point adsorption of an olefin would take place with an angle of 112° for the Mo—C—C bonds. This fit is not

quite so good as on molybdenum dioxide and therefore does not explain the greater activity of MoS_2 .

It must be remembered that an important step in the destructive hydrogenation process is a reduction in the molecular weight of the hydrocarbons. This involves rupture of a C—C bond.

Now, although the mechanism of this breakdown is probably very similar to that of hydrogenation of a double bond, involving two-point adsorption of adjacent carbon atoms, it is more exacting in its requirements of spacings on the catalyst surface. If the adsorbed molecule is a paraffin, its attachment to the surface involves simultaneous loss of two hydrogen atoms and four adjacent sites on the catalyst are required; only if two other hydrogen atoms are also available on other adjacent sites will the C—C link be broken and two separate molecules desorbed by taking up two hydrogen atoms each. The whole operation therefore requires six adjacent sites. When there is a deficiency of hydrogen atoms, the larger molecule may be desorbed only as unchanged paraffin, or may even lose hydrogen to produce an olefin. This reasoning suggests that the higher activity of MoS_2 can be attributed partly to the greater number of molybdenum atoms in close proximity compared with those in the best plane of MoO_2 . Perhaps also differences in the activation energy of hydrogen adsorption are involved. The observed behavior of a catalyst whose character is largely dependent on geometrical factors with respect to one reactant may therefore be equally dependent on the adsorption of a second reactant which is held by single point attachment.

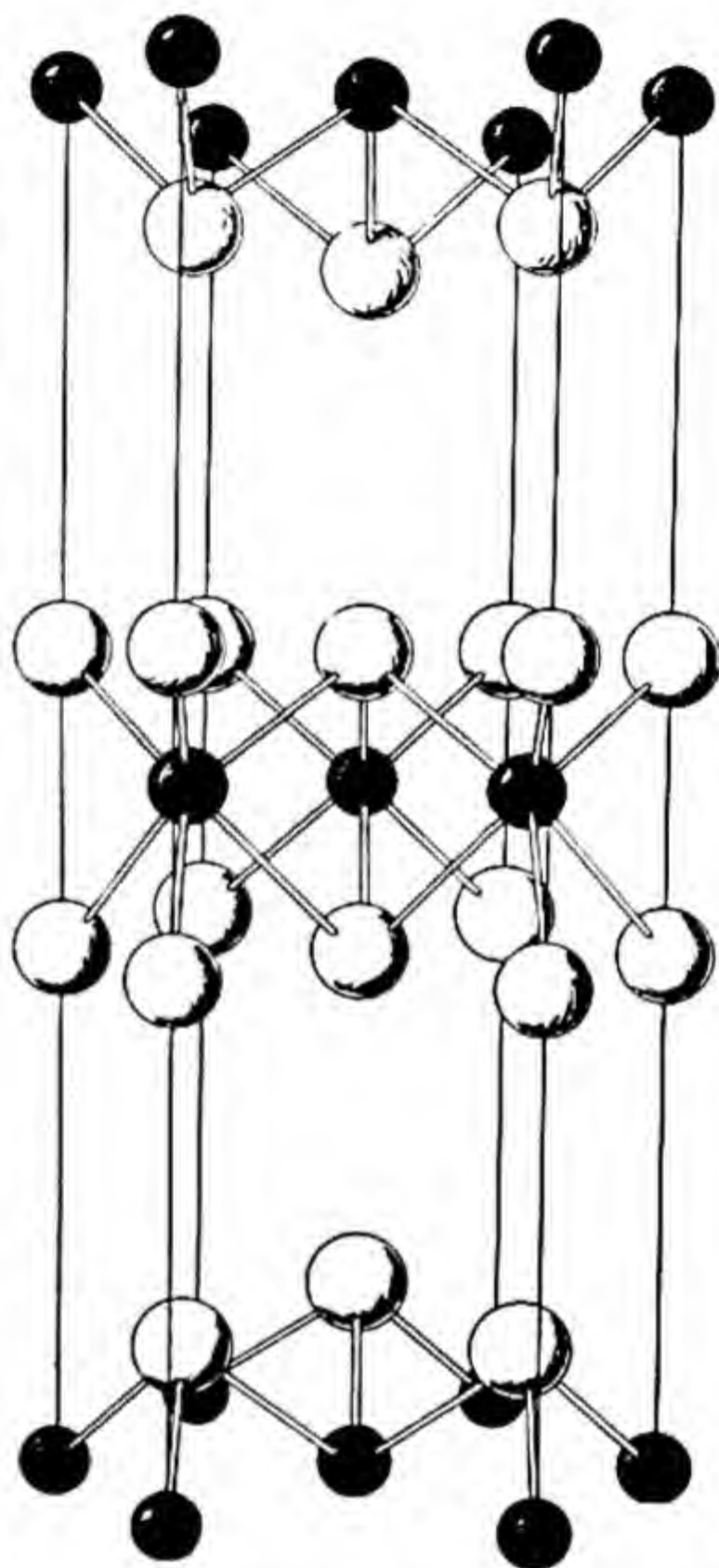


FIG. 8. The MoS_2 crystal, showing incomplete cells with molybdenum layers exposed.

VII. THE REACTIONS OF HETEROCYCLIC COMPOUNDS

Calculations similar to those given above may be extended to organic compounds other than hydrocarbons; for example, in the series furan,

thiophene, and pyrrole, hydrogenation catalysts can be found which will lead either to the formation of the corresponding tetrahydro derivatives or to much more extensive breakdowns with removal of the heteroatom as water, hydrogen sulfide or ammonia.

Reference to the bond angles and interatomic distances for these molecules shows that as far as the carbon atoms are concerned their values are little different from those of the olefin molecule. It would be expected, therefore, that catalysts which were effective for hydrogenation of the latter would also function with the heterocyclic molecules. This is found to be so, in that nickel catalysts are known to give tetrahydrofuran and pyrrolidine by the hydrogenation of furan and pyrrole at 180° (Padoa, 25). Tetrahydrofuran is also formed by the use of platinum (Starr and Hixon, 26), osmium, or palladium (Shuikin, Nikiforov, and Stolyarova, 27) as the catalyst, and pyrrolidine is similarly produced by palladium or rhodium catalysts (Zelinskii and Yurev, 28). In all these metals there are spacings of the atoms very similar to those in metallic nickel, the hexagonal osmium lattice having a equal to 2.71 Å.

The corresponding change with thiophene does not take place because the catalysts are poisoned by the sulfur. In order to hydrogenate thiophene, therefore, sulfur-resisting catalysts must be sought. These have been found in the sulfides of molybdenum and nickel, described by Moldavskii and Kumari (29) and by Cawley and Hall (30). In both these series of experiments, static systems under pressure were used, so that no sulfur was carried away from the reaction zone and at least part of the catalyst remained in the form in which it was originally added. The structures of MoS_2 and NiS are therefore to be considered.

What has already been said about the disposition of olefins on MoS_2 can obviously be applied equally to the thiophene molecule, assuming that one double bond is opened by two-point adsorption. This argument, which can explain the known activity of MoS_2 for this conversion, would also indicate a similar activity for NiS , since this sulfide consists of a hexagonal lattice with alternate layers of nickel and sulfur atoms in which the shortest Ni—Ni distance is 2.65 Å., and which would, therefore, be suitable for two-point adsorption of thiophene.

When the reactants are flowing continuously over the catalyst, however, nickel sulfide no longer remains effective because NiS is not stable in contact with hydrogen at temperatures above 150° . It is changed into the subsulfide, Ni_3S_2 , which has a rhombohedral structure and a unit cell edge of 4.04 Å. (Westgren, 31). No pairs of nickel atoms exist on the 100-plane of this crystal at or near the correct spacing to give two-point adsorption of thiophene. On the 111-plane, groups of three nickel atoms are present, as shown in Fig. 9, in a triangular arrangement, and any pair of these would

give the correct distance for the required adsorption of the organic molecule, but do not provide for the additional two hydrogen atoms also needed. Nickel subsulfide, therefore, is an effective catalyst for the hydrogenation of carbon disulfide and other simple organic sulfur compounds which are held

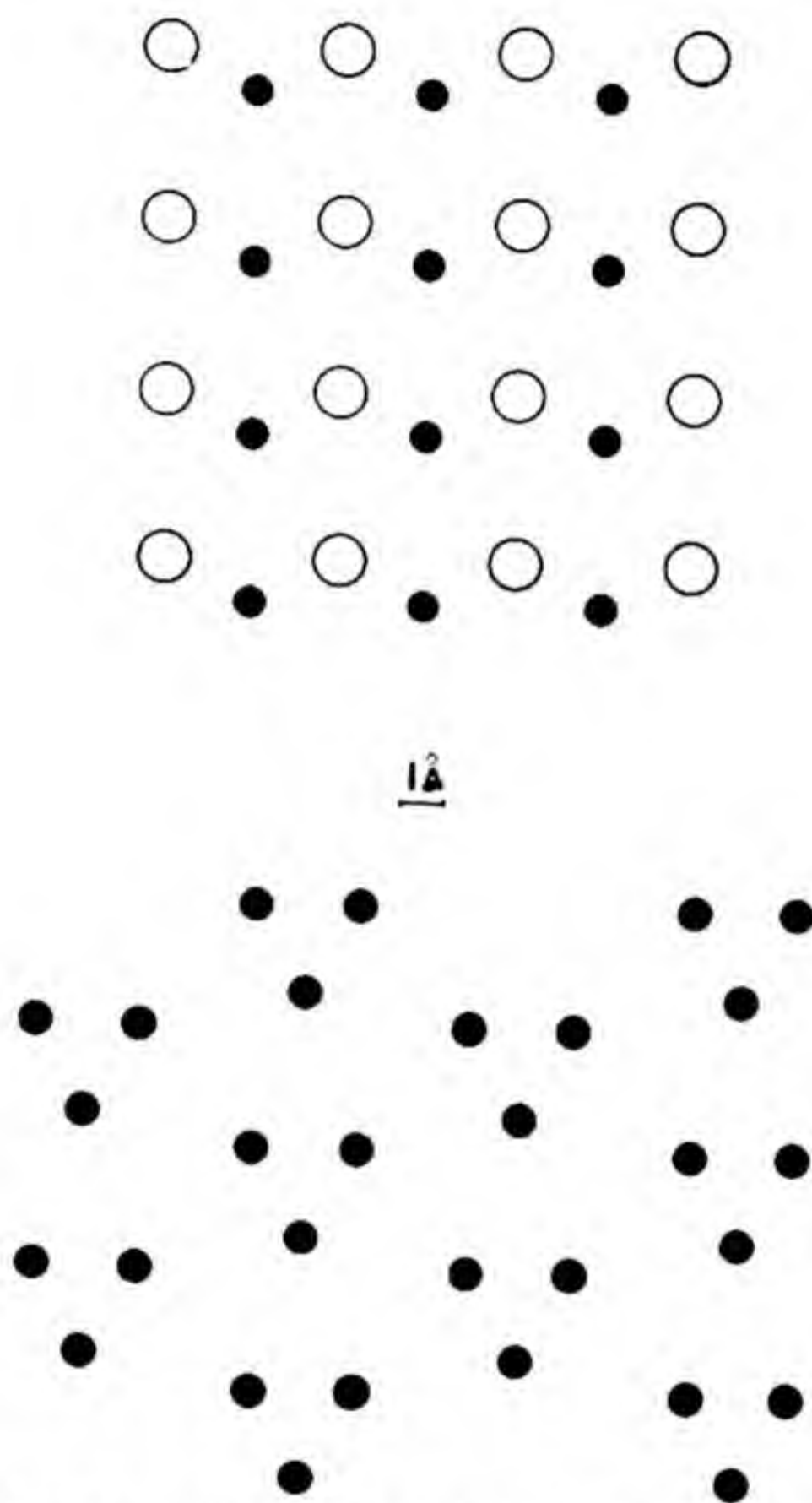


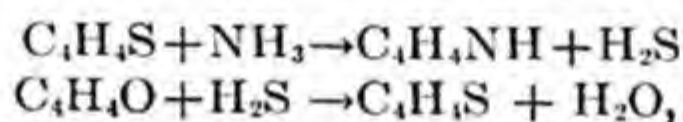
FIG. 9. Nickel subsulfide. Plans of the 100-plane (upper) and of the 111-plane (lower).

by single-point adsorption (Crawley and Griffith, 32) but not for the destructive hydrogenation of organic molecules.

These observations emphasize the fact that direct measurement of the separate adsorption of thiophene and of hydrogen on this catalyst would not disclose this important feature. Determinations of this kind must be used with caution in the prediction of results to be expected when multi-point adsorption is involved.

In spite of the fact that nickel subsulfide does not produce tetrahydrothiophene, it is possible to decompose thiophene into hydrogen sulfide and butene by passage over this catalyst at about 400°. The mechanism of this breakdown, however, is entirely different from any of those discussed above and depends on the reaction of the sulfur atom with metallic nickel which is formed when nickel subsulfide is treated with hydrogen at temperatures above 350° (Griffith, Marsh, and Newling, 33). But a geometrical factor may also be involved even in this breakdown of thiophene. While this reaction proceeds smoothly in pure hydrogen, the conversion is completely inhibited in coal gas. The reason for this failure is not that the simpler olefins in the coal gas are competing with the thiophene, but that cyclopentadiene is strongly adsorbed and polymerized, to the exclusion of the far less plentiful thiophene. Several other substances which are only held by single-point attachment are also contributing to the covering of the surface; for example, carbon disulfide has been found to retard the conversion of thiophene in hydrogen.

In studying this series of changes, it is interesting to note that the heteroatom appears to have little influence on the alignment of the molecule. This is not always so, and the same group of heterocyclic compounds can take part in an entirely different set of reactions such as:



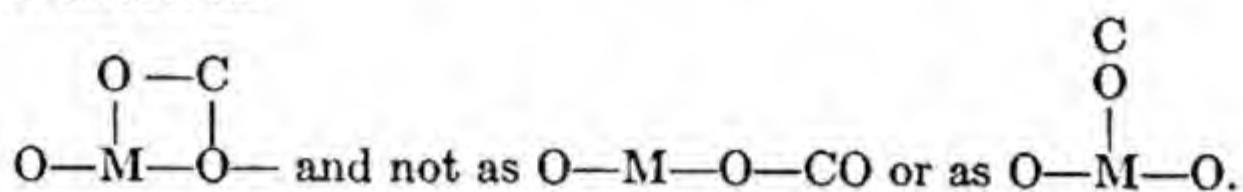
similar changes occurring rather more readily with the tetrahydro derivatives in contact with alumina catalysts at 400–450° (Yurev, 34). It is possible that two-point attachment of the heteroatom and of one carbon atom may be involved in this type of conversion.

VIII. THE OXIDATION OF CARBON MONOXIDE

None of the systems so far considered has involved oxygen as one of the reactants, and in fact very little is yet known about the effect of geometrical factors in oxidation. One example can be found in the Hopcalite reagents and catalysts described by Pitzer and Frazer (35). They have shown that the higher oxides of cobalt, nickel and manganese, which are effective for oxidation of carbon monoxide, have all metal-oxygen bond lengths very similar to one another; thus for MnO_2 the bond length is 1.84 Å., for Ni_2O_3 , 1.84 Å., for Co_2O_3 , 1.85 Å., and for Co_3O_4 , 1.75 Å. Copper oxide with a bond length of 1.87 Å. is not itself active but functions as a promoter. Other important features of the process are (1) that carbon monoxide can undergo activated adsorption on other catalysts which do not effect the oxidation reaction, (2) that carbon monoxide can be oxidized on inactive

forms of manganese oxide but the process is not catalytic, and (3) that poisoned catalysts have increased coordination round the metal atom.

These facts indicate that the carbon monoxide must be held simultaneously by both metal and oxygen atoms. Thus, the adsorbed molecule must be represented as



After the loss of CO_2 the manganese oxide is reoxidized.

In any further study of the geometry of these surfaces, it would be instructive to determine the exact crystallographic species involved in the truly catalytic stage. Alekseevskii and Frid (36) state that only the α -form of MnO_2 is active for the oxidation of carbon monoxide, and recent work by Feitknecht and Märti (37) has provided new knowledge concerning the higher oxides of manganese and the manganites. For example, they have shown that manganous manganite and the manganites of other divalent metals have a double layer lattice in which planes of MnO_2 with hexagonal symmetry are separated by disordered layers of the hydroxide of the lower valency metal. The disorder of the intermediate planes lies in their incompleteness, and a very small proportion of these hydroxides is sometimes sufficient to stabilize the whole structure. It seems probable that the unique properties of the Hopcalite catalysts are dependent on this structure. Interpretations rather similar to those described above may be placed on results observed by Eckell (38). Carbon monoxide was oxidized by contact with catalysts consisting of ferric oxide to which varying amounts of alumina had been added. It was shown that a quantitative relationship existed between the interatomic distances in the catalyst, which decreased as the content of Al_2O_3 increased, and the activation energy for the oxidation. Beyond the miscibility gap at 25% Al_2O_3 , both retained a steady value. It is possible, however, that in a system of this type, where reduction of Fe_2O_3 to Fe_3O_4 is known to occur to a recognizable extent, the effects depend on factors other than the actual spacing of the reacting molecules on the surface. The subject is one which lends itself to extended investigation and is closely related to the problems of promoter action.

IX. FUTURE DEVELOPMENT

It will be evident, from the limited number of items discussed above, that the study of the geometry of catalytic surfaces and of molecules adsorbed on them is in a very early stage of development. It may, therefore, be useful to indicate a few directions in which further practical and theoretical advances may be expected. In extending the examination of catalysts,

it is highly desirable that more attention should be given to evaporated films of sulfides and oxides, which can be prepared by methods similar to those already used with metals. The determination of the structure of such films by electron diffraction and by microscopic examination, and the measurement of their surface areas, could then be related to their adsorptive capacities and catalytic activities under a variety of conditions.

On the theoretical side also, importance must be attached to oxides and sulfides because these present many problems which do not arise with metallic catalysts. The function of the oxygen and sulfur atoms in such lattices is a matter of prime importance, and structures produced by partial removal of these elements from their compounds must have very special properties. It would be of great interest to know, for example, in what positions the hydrogen atoms split off during ring-closure of aliphatic hydrocarbons are adsorbed on the catalyst; it seems highly probable that the oxygen atoms in the chromium oxide or molybdenum oxide are involved and that they contribute an essential part to the specific effects of these catalysts.

There is a wide range of cracking and isomerization reactions involving many types of hydrocarbons whose mechanism is not understood, but which must be closely related to the structure of the catalyst surface. Owing to the complicated character of the catalyst used for some of these processes, and to the occurrence of side reactions leading to fouling by heavy polymers, there are several practical difficulties to be overcome in solving such problems. As far as oxidation reactions are concerned, much less information is available.

In many instances, as, for example, in the production of ethylene oxide by oxidation of ethylene with silver catalysts (Twigg, 39), the reaction takes place by collision with chemisorbed oxygen. It is, however, quite likely that instances will be found where the mechanism is entirely different and where two-point adsorption takes place.

In most existing discussions on the geometrical factor, attention has been focused exclusively on the demands of the carbon bonds, and those of the elements in the catalyst surface have been ignored. As long as the crystal lattice has an ionic structure, this is permissible, but it is quite clear that with other structures, such as that of molybdenite, this procedure is unsatisfactory. If the position of an olefin adsorbed by two carbon atoms is considered at right angles to the Mo plane of MoS_2 , the angle $\text{Mo}-\text{C}-\text{C}$ would be 112° if $\text{Mo}-\text{C}$ is 2.14 Å., $\text{Mo}-\text{Mo}$ is 3.15 Å. and $\text{C}-\text{C}$ is 1.54 Å. The $\text{C}-\text{Mo}-\text{Mo}$ angle, therefore, should be 68° . Now the $\text{S}-\text{Mo}-\text{S}$ angles in the crystal are either 82 or 136° , of which the smaller is the one available above a bare plane of Mo atoms; the bond angle above the plane is 41° , and the olefin must, therefore, be held in a tilted position. It should

be possible to relate an effect of this kind to the capacity of a known surface for adsorption of a hydrocarbon.

These few suggestions will indicate that a better knowledge of the geometrical factors in catalysis can only be obtained by the combined results of several distinct methods of theoretical and practical treatment. One of the most important of these is to increase the information available about the nature of the bond between the adsorbed molecule and the catalyst, and about its dependence on the chemical properties of the catalyst elements.

In this article, no account has been included of the evidence provided by work on promoter actions or on catalyst poisons. Both these have made contributions to the study of the geometrical factor, and are likely to do so more extensively in the future, but these subjects are themselves of such importance in any report on catalysis that they should be the subject of a separate treatment.

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The Fischer-Tropsch and Related Processes for Synthesis of Hydrocarbons by Hydrogenation of Carbon Monoxide*

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I. INTRODUCTION

Industrial and scientific development of the chemistry of carbon monoxide hydrogenation has increased in direct proportion to the growth of the art of contact catalysis. To such earlier processes as the water-gas shift, the reduction of carbon monoxide to methane, and the synthesis of methanol, recent developments have added the synthesis of normal and isoparaffins and C_4 to C_{20} normal and branched-chain alcohols. Research on carbon monoxide hydrogenation at very high pressures has barely begun but has already yielded the synthesis of paraffin waxes of very high molecular weight which are not found in natural petroleum. The synthesis of polyhydric alcohols at very high pressures of hydrogen and carbon monoxide remains as one of the prizes of further research.

II. DEVELOPMENT OF THE RUHRCHEMIE PROCESS

In 1913, the Badische Anilin und Soda-Fabrik (1) disclosed that hydrogen and carbon monoxide would react at 100–200 atmospheres pressure in the presence of alkali-activated cobalt or osmium oxide supported on asbestos to form a liquid product containing alcohols, aldehydes,

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ketones, fatty acids, and some saturated and unsaturated aliphatic hydrocarbons. This work led eventually to the development of the methanol synthesis by the same company. In 1923, Franz Fischer and Hans Tropsch (2), working in the Fuel Research Laboratories of the Kaiser Wilhelm Institute, found that alkalized iron turnings catalyzed the production of an oily liquid from hydrogen and carbon monoxide at 100–150 atmospheres pressure and 325–425° C. This product was called synthol, and it contained alcohols, acids, aldehydes, ketones, esters, and hydrocarbons. Fischer and Tropsch found that, at lower pressures of about 7 atmospheres, the oil obtained was almost completely paraffinic and contained a small fraction only of oxygenated organic compounds. At the lower pressure, however, only a very low yield of oil was obtained. In 1925–1926, Fischer and Tropsch (3, 4) developed much more active catalysts for the synthesis; these consisted of promoted cobalt, iron, or nickel. Use of these catalysts provided a fair yield of oil even at 1 atmosphere pressure, with only minor amounts of oxygenated organic compounds in the product, which was labeled "kogasin." Experimental work with Co-MnO-Cu and other catalysts was reported by Elvins and Nash (5, 6) in England in 1926–1928 and by Smith, Davis, and Reynolds (7) of the United States Bureau of Mines.

In 1928–1929, Fischer, Tropsch, and Koch (8, 9, 10) published the results of an analysis of the oil product from an Fe-Cu catalyst operated at atmospheric pressure and 250° C. The fraction boiling in the range 60–185° C. was 70% olefinic. The 30% saturates contained octane, nonane, and isonane; no diolefins or naphthenes were found. Minute amounts (0.1–0.4%) of benzol and toluol were present. The isononane was probably 3-methyloctane and was present in very small amount. A very small amount of 3,3-dimethylpentene-1 also was present. In 1928, an analysis was published by Smith, Hawk, and Reynolds (11) of the product from a Co-Cu-MnO catalyst. This product, although more saturated, was similar to that obtained by Fischer and his coworkers from an Fe-Cu catalyst. In 1930–1932, Kodama and other Japanese experimenters (12, 13, 14, 15) published data on the efficiency of different promoters such as Cu, ThO₂, WO₃, MoO₃, MgO for the cobalt catalyst.

In 1930, Smith, Hawk, and Golden (16) discovered that ethylene, when added to the synthesis gas, enters into the oil-producing reaction on a Co-Cu-MnO catalyst but not on an Fe-Cu catalyst. In the latter case, most of the ethylene appears as ethane in the products. It was pointed out also that water was the main oxygenated product from the cobalt catalyst, whereas carbon dioxide was the chief corresponding product on the iron catalyst. The behavior of ethylene when added to synthesis gas and passed over a cobalt catalyst was verified by Craxford (17) in 1939.

Storch (18) reported data on C_1 to C_2 ratios in the end gases from the synthesis as follows: 10:1 on promoted cobalt, 4.5:1 on unpromoted iron, and 1:2 on iron-copper catalysts. Any postulated mechanism of the synthesis should provide a satisfactory explanation of these facts concerning the function of ethylene in the reaction.

In 1930-1932, Fischer and his coworkers (19, 20, 21) developed more active promoted nickel and cobalt catalysts, and increased the yield per pass to over 100 g. oil/cubic meter of $2 H_2 + 1 CO$ gas. In 1932, Fischer and his coworkers (22, 23, 24, 25, 26) started process development work, using a Ni-MnO- Al_2O_3 -kieselguhr catalyst. Because of the highly exothermic character of the reaction, he found it essential that the path of heat transfer from a granule of catalyst to a cooling surface be less than 10 mm., preferably about 7 mm. His first experimental plant consisted of a battery of cells 12-mm. thick by 1.2-meters wide by 5-meters high, immersed in an oil bath. A yield of 70 g. oil/cubic meter of $2 H_2 + 1 CO$ was obtained at 190-210° C. and at atmospheric pressure. In 1933, the Ruhrchemie A.G. (27, 28, 29, 30, 31) erected a pilot plant of about 1000 tons/year capacity at Oberhausen-Holtien. A Ni-MnO- Al_2O_3 -kieselguhr catalyst was used at 190-210° C. and at atmospheric pressure. The difficulties encountered (32) were a short catalyst life of 4-6 weeks, despite an elaborate and expensive sulfur-removal process, expensive design of converters, loss of catalyst metals and promoters during catalyst regeneration, and conversion of kogasin to marketable products.

In the period 1933-1939, an intensive and rapid development of more active catalysts occurred, with final selection of Co-ThO₂-MgO-kieselguhr (100:5:8:200 parts by weight) as the best catalyst for industrial operation (33, 34, 35, 36). Table I (37) contains the results of laboratory tests at 1 atmosphere and at 7 atmospheres pressure, using this catalyst.

Koch and Hilberath in 1941-1942 (38, 39) studied the composition of the fraction of the product from the cobalt catalysts which boiled below 100° C. The saturated C_4 fraction contained 7.5% isobutane. The remainder of the product fraction boiling below 100° C. contained, in addition to nC_5 , nC_6 , and nC_7 , also methylbutane, 2-methylpentane, 3-methylpentane, 2-methylhexane, and 3-methylhexane. Only traces of more highly branched paraffins were found. In 1939, von Weber (40) had estimated the degree of branching of different fractions of the product from measurements of the boiling points and molecular weights of fractions of Fischer-Tropsch gasoline and reported:

Fraction	C_6	C_7	C_8	C_9	C_{10}
Mol fraction of branched hydrocarbons	0.15	0.20	0.27	0.35	0.40

These data show that 1 out of every 25 to 50 carbon atoms of the C_6 to C_{10}

fractions is a tertiary carbon. No quaternary carbon was found in either von Weber's or Koch and Hilberath's work. In the Bureau of Mines, a recent infrared spectrometric analysis of the C_6 fraction from a cobalt catalyst showed 10% 2-methylpentane and 5% 3-methylpentane.

TABLE I

*Product from 100 Co:5 ThO₂:7.5 MgO:200 Kieselguhr
Catalyst at 175–200° C. and at (A) Atmospheric,
(B) 7 Atmospheres Pressure of 2H₂ + 1CO Gas, 18–20% Inerts. No Recycle.*

Fraction	Ideal gas, g./m. ³		Weight % of liquids plus solids		Density, 150° C.		Olefins, volume %		Pour point, ° C.		CFR octane number		Cetene number	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
C ₁ +C ₂	26	21
C ₃ +C ₄	24	17	50	30
C ₄ to C ₁₀	70	51	56	35	0.689	0.685	37	20	52	28
C ₄ to C ₁₁	77	58	62	40	.693	.689	34	18	49	25
C ₁₁ to C ₁₈	41	51	33	35	.760	.760	15	10	-18	-7	100	100
C ₁₂ to C ₁₉	34	51	27	35	.766	.766	13	8	-9	-2	100	105
Soft wax	10	36	8	25	.900	.900
		to												
Hard wax	4	43	3	30	.930	

^a Higher percentage of wax may be obtained from Co-Mn catalysts at 165–168° C. and 10 atmospheres, but with no increase in Diesel oil yield.

All of the German Fischer-Tropsch plants in 1938–1944 (41–49) were operating according to the Ruhrchemie process using the Co-ThO₂-MgO-kieselguhr catalyst at 180–200° C., at either 1 or 10-atmospheres pressure, and with 2 or 3 stages with product recovery after each stage. The average yield was 150 g./cubic meter of 2H₂+1CO gas of hydrocarbons ranging from propane-propylene to waxes of 2000 molecular weight. The space velocity employed was 60 to 100 volumes of feed gas/volume catalyst space/hour.

The normal synthesis gas required for the Fischer-Tropsch process is a mixture of 2 volumes of hydrogen and 1 volume of carbon monoxide. Recent practice in the Ruhr when using cobalt catalyst showed ratios of from 1.8 to 2.0 for the atmospheric pressure process and ratios as low as 1.5 for the medium-pressure process. In the Ruhrchemie plant at Sterkrade, the medium-pressure process used different ratios for each of the three stages of the synthesis, 1.4, 1.6, and 1.8, respectively, by introducing the requisite amount of "converted" water gas before each stage. In all cases, the synthesis gas contained inert constituents which seldom exceeded 20% by volume.

In all plants in the Ruhr, synthesis gas was manufactured from coke in standard design "blue-water" gas generators. In a few plants, this process was supplemented by other processes such as cracking of coke-oven gas. In order to obtain the higher ratio of hydrogen to carbon monoxide required for the standard Fischer-Tropsch operation, it was necessary to pass a portion of the water gas, mixed with an excess of steam, through converters containing a "shift" catalyst whereby carbon monoxide was converted into hydrogen and carbon dioxide. An iron oxide-chromium oxide catalyst was used in this step at 450–500° C. In two plants in the Ruhr, a high-hydrogen gas was produced by cracking or re-forming coke-oven gas, and the product was mixed with water gas, thereby reducing the volume of water gas to be converted.

At the Krupp Fischer-Tropsch plant at Wanne-Eickel there was a large commercial installation of the Krupp-Lurgi process for manufacture of low-temperature coke. Most of this coke was gasified in blue-water-gas machines and yielded a hydrogen to carbon monoxide ratio of 1.35, which is closer to the desired ratio for synthesis than is obtained from high-temperature coke. Several processes for the complete gasification of coal were developed in Germany, and, although they were used for production of hydrogen for coal hydrogenation or synthetic ammonia production, the same plants, with only minor modifications, could have made synthesis gas. The Pintsch-Hillebrand, the Schmalfeldt-Wintershall, and the Winkler were three such processes.

The Fischer-Tropsch process requires synthesis gas in which the total sulfur does not exceed 2.0 mg./cubic meter. This purification was done in two stages: (1) Removal of hydrogen sulfide and (2) removal of organic sulfur. The removal of hydrogen sulfide is almost universally carried out by the well known iron oxide process. At the Luetzkendorf plant, the so-called "Alkazid" process had been installed, in which a solution of an alkaline organic compound absorbs the hydrogen sulfide, which is then continuously stripped from the solution by steam. At Luetzkendorf, the evolved hydrogen sulfide was converted into elemental sulfur.

Organic sulfur was removed in all of the German Fischer-Tropsch plants by passing the synthesis gas through an alkalized iron oxide catalyst (containing about 30% sodium carbonate) at 280° C. The reaction is essentially catalytic oxidation of the organic sulfur in the gas, and it is necessary that a small percentage of oxygen be present in the synthesis gas.

The details of preparation and reduction of the Co-ThO₂-MgO-kieselguhr catalyst are described in CIOS reports (41–49) and other publications (34, 35, 36). A solution of cobalt and thorium nitrates is mixed with sodium carbonate solution so as to completely precipitate the cobalt and thorium carbonates. A slurry of magnesium oxide and kieselguhr is

mixed with the suspension of cobalt and thorium carbonates, the mixture rapidly filtered, washed exhaustively, and the filter cake dried. It is then crushed and screened to obtain 1- to 3-mm. granules. These are reduced at 350–450° C. in a stream of dry carbon dioxide-free hydrogen flowing at a space velocity of 3000 to 4000 volumes/volume of catalyst. The reduced granules are stored in an atmosphere of carbon dioxide in steel containers used to ship the catalyst to the synthesis plants.

The converters in atmospheric pressure Fischer-Tropsch plants consist of rectangular steel boxes about 15-feet long, 8-feet high, and 6-feet deep. These contain vertically placed steel sheets about 2-mm. thick, spaced about 7 mm. apart. The spaces between the steel plates contain the catalyst. The steel sheets are perforated by horizontally placed cooling pipes about 5-cm. o.d., through which water under pressure is circulated. The cooling tubes are manifolded and connected to a steam boiler which generates steam for power and heating purposes. The converters in the medium-pressure (10–15 atmospheres) Fischer-Tropsch plants are essentially similar to tube boilers, except that the tubes are double, with the catalyst contained in a narrow annulus between two concentric tubes. A top and bottom weld through the outer tube connects the inner tube with the boiler space, so that it is filled with cooling water. The annular layer of catalyst has an inside diameter of 24 mm. and an outside diameter of 44 mm. and is 15-feet high. Each converter contains about 2000 such tubes welded into tube sheets and is about 8-feet in diameter. The weight, volume, cooling surface, and capacity of the atmospheric- and medium-pressure converters are listed in Table II. Table III shows the number of converters in different stages at several of the German plants.

TABLE II
Ruhrchemie Converter Characteristics

Characteristic	Atmospheric pressure	Middle pressure
Weight (tons)	45	45
Volume (total) cu. ft.	650	950
Volume (catalyst) cu. ft.	350	350
Finned surface sq. ft.	38700	None
Tube surface sq. ft.	4300	22600
Capacity barrels of primary product per day	18	18

Rheinpreussen at Moers operated 96 conventional Ruhrchemie atmospheric pressure reactors, of which 60 were normally in the first stage and 30 in the second stage. The operating temperature was in the range 195–

200° C. The synthesis-gas charging rate averaged about 630 cubic meters/hour/oven. The total liquid product, including "Gasol" (C_3 and C_4),

TABLE III

Multi-Stage Operation at Several German Plants

Name	Location	Number of converters			Pressure, atm.
		Stage 1	Stage 2	Stage 3	
Hoesch-Benzin	Dortmund	40	16-20	4-8	10-15
Ruhrbenzin	Sterkrade	36	18-20	14	11
			48 Total		1
Rheinpreussen	Moers	60	30	0	1
Klocknerwerke	Castrop-Rauxel		63 Total		1

averaged 150-155 g./cubic meter. The product distribution is shown in Table IV.

TABLE IV

Rheinpreussen Product Distribution

Constituent	Per cent
Gasol ($C_3 + C_4$)	10.0
Gasoline	52.2
Diesel oil	26.5
Soft paraffin wax	7.6
Hard paraffin wax	3.7

Ruhrbenzin at Sterkrade-Holten operated about 48 atmospheric-pressure reactors and 72 middle-pressure reactors, all of conventional design. The normal pressure ovens are operated in two stages on charge gas containing the usual 2 volumes of hydrogen and 1 volume of carbon monoxide. The arrangement of the middle-pressure reactors is shown in Fig. 1 (42). In this operation, the H_2 to CO ratio of the inlet gas to the three stages is adjusted to 1.4, 1.6, and 1.8, respectively, by introducing the requisite amount of converted water gas before each stage.

For Stage 1 of the medium-pressure operation, the inlet gas rate is 1000 cubic meters/hour/oven, the temperature 180-200° C., and the gas contraction 50%. Similar conditions obtained for Stage 2. In Stage 3, where all newly charged ovens are started, higher rates, namely, 2000 cubic meters/hour/oven, and lower temperatures, 165-185° C., can be employed. The over-all contraction is about 75% and the yield, 150 g. C_3 and higher hydrocarbons per cubic meter of ideal gas (that is, $2H_2 + 1CO$). The

advantage of starting with a gas relatively deficient in hydrogen and then increasing the proportion of hydrogen in later stages lies in combining the beneficial effects of low hydrogen partial pressure on olefin content and

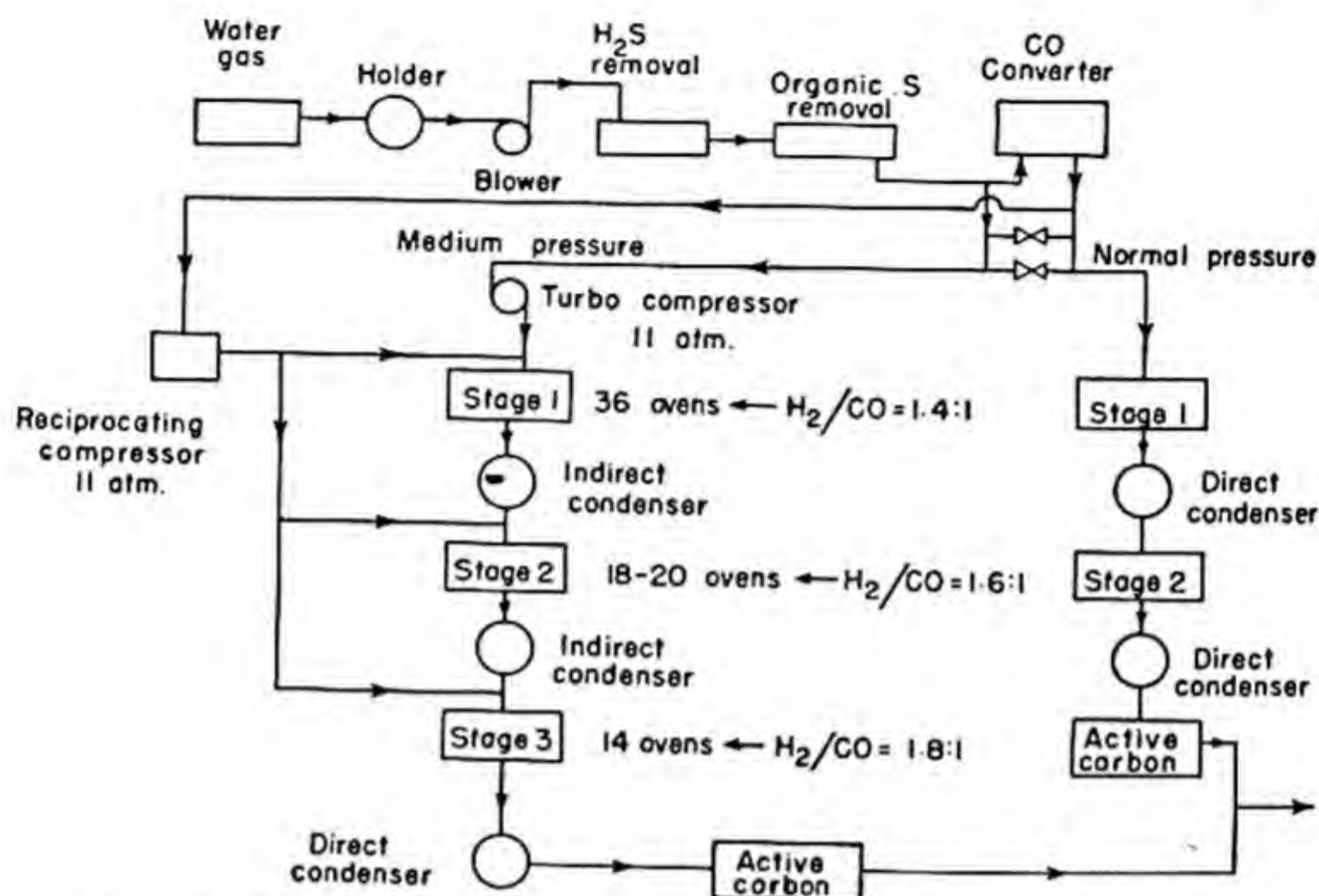


FIG. 1. Flow scheme for synthesis cycle used at Sterkrade.
(Ruh Chemie, A.G.-Ruhrbenzin A.G., Sterkrade)*

* Figures 1-11 published by courtesy of the Bureau of Mines, U. S. Department of the Interior.

methane production with the efficient utilization of the carbon monoxide achieved with normal synthesis gas ($2\text{H}_2:1\text{CO}$).

The products produced by this method of operation are shown in Table V.

TABLE V
Product at Ruhrbenzin, Sterkrade-Holten

Product	Weight, % total product	Per cent of olefins in fraction
Gasol ($\text{C}_3 + \text{C}_4$)	10	40
C_5 to $170^\circ \text{C}.$ ^a	25	24
$170-280^\circ \text{C}.$	30	9
$280-340^\circ \text{C}.$ (soft wax)	20	..
Residue (hard wax)	15	..

^a Motor octane number, about 45.

When normal synthesis gas ($2\text{H}_2 + 1\text{CO}$) is used throughout, 14% of the total hydrocarbons produced is methane, but with the above scheme, the proportion is reduced to 10%. The middle-pressure synthesis yields 2 to 3 times as much wax as the synthesis at atmospheric pressure.

III. DEVELOPMENT OF FISCHER-TROPSCH PROCESSES OTHER THAN THE RUHRCHEMIE PROCESS

All of the commercial German Fischer-Tropsch plants in 1938-1944 were operating the Ruhrchemie process, using a cobalt-thoria-magnesia-kieselguhr catalyst at about 200° C. either at 1 or 10 atmospheres pressure, and with two or three stages with product recovery after each stage. The only outstanding process development using the cobalt catalyst consisted in recycling about 3 volumes of end gas from the first stage per volume of fresh gas with product condensation after each cycle (41-53). On a pilot-plant scale, this development resulted in an increase of 30% in the throughput without sacrifice in yield per cubic meter of $2\text{ H}_2 + 1\text{ CO}$ gas, or in an increase of the yield from 150 to 170 g./cubic meter at the same throughput. Using the recycle process and charging water gas ($1\text{ H}_2 + 1\text{ CO}$) instead of $2\text{ H}_2 + 1\text{ CO}$, the olefin content was increased from 20 to 55% in the liquid fractions of the product. When water gas is used in the older process without recycling, a low catalyst life results because of carbon deposition. The recycle gases lower the partial pressure of the carbon monoxide sufficiently to avoid excessive carbon formation. The recycle-process gasoline has a 50-55 motor octane number as compared with 45 for the older process without recycle. Refining the gasoline from the recycle process by passage over activated clay increases the octane number to 70 without appreciable decrease in yield. The cetane number of the fraction boiling from 120 to 280° C. was above 100.

The Lurgi and I. G. Farben companies were active during 1938-1944 in process development using iron catalysts (50, 53). I. G. Farben operated a pilot plant using a sintered iron catalyst and a hot-gas recycle process. The catalyst was prepared by making a paste of iron powder (obtained by decomposition of iron carbonyl) with a dilute solution of sodium borate. The extruded and dried granules were heated in a hydrogen atmosphere at 850° C. for several hours before use in the synthesis, which was conducted in the range 320-330° C., 20 atmospheres, and $\frac{3}{4}$ -second contact time. The gases from the converter were recycled through a heat exchanger to remove heat of reaction. Conversion per pass was about 1%, so that about 100 volumes of recycle gas to 1 of fresh gas entered the converter.

The gas is passed over the catalyst so rapidly that the temperature does not rise beyond the optimum upper limit (about 350° C.). The heat evolved in the synthesis (about 4000 kcal./kg. of product or 7200 B.t.u./pound) is absorbed in an external heat exchanger, using a 10° C. drop in temperature of the recycle gas. The conversion is about 1%/pass; therefore, 1% of fresh synthesis gas is added per cycle, and an equivalent amount of gas from the reactor is removed and passed through a condensation and product recovery system and thence to a second stage, which is about

one-quarter the size of the first stage. In between the two stages, the gases are cooled to 0°C . and carbon dioxide is scrubbed out. All of the available yield data are extrapolations of results obtained in a single stage in a pilot plant operated for several months using 400 l. of catalyst, and a hydrogen to carbon monoxide ratio of about 0.9. The conversion in the first stage was 78%, and the conversion in a second stage was estimated at $13\frac{1}{2}\%$. The yield per cubic meter of fresh gas was about 160 g. hydrocarbons, of higher molecular weight than ethane. The space-time yield was about 1 kg. of product/l. of catalyst/day (this is about eight times that from the Ruhrchemie cobalt catalyst process). The products were reported to contain:

1. 44% unrefined highly olefinic gasoline of 75–81 research octane number. Upon refining, a 90% yield of 84–86 research octane number gasoline was obtained.
2. 11% Diesel oil of 47–53 cetene number and -25°C . pour point.
3. 7% C_4 and 8% C_3 . (The C_3 and C_4 were 80% unsaturated.)
4. 5% C_2H_4 .
5. 17% $\text{CH}_4 + \text{C}_2\text{H}_6$.
6. 7% alcohols, chiefly ethanol and propanol.
7. 1% paraffin wax.

This report is remarkable in that only 17% methane plus ethane is specified. Others who have experimented with iron catalysts at $300\text{--}320^{\circ}\text{C}$., with little or no recycle of end gases, have reported much higher yields of methane and ethane. The cost of operation of this process is markedly dependent upon the pressure drop across the catalyst bed. This was reported to be 1 meter water/meter of catalyst depth. Increased gradients would result with increasing carbon deposition, and the operating temperature is dangerously close to that at which a rapid rate of carbon formation occurs.

Other processes in the development stage by I. G. Farben included a liquid-phase operation in which iron powder prepared from iron carbonyl is mixed with a high-boiling oil and synthesis gas bubbled through the mixture. This process yields more Diesel oil (of 60–70 cetene number) and much less methane and ethane than the hot-gas recycle process. The gasoline from the liquid-phase process operated at about 300°C . is reported to have a research octane number of 90. Another I. G. Farben development was an oil-recycle process in which a cooling oil was passed concurrent with the synthesis gas over granules of an iron catalyst (synthetic ammonia type, $\text{Fe}_3\text{O}_4 + 2.5\%\text{Al}_2\text{O}_3 + 0.5\%\text{K}_2\text{O}$). The cooling was effected by recycling the heated oil through an external heat exchanger.

Development work by the Lurgi Company (21) involved a recycle

operation using a Ruhrchemie middle-pressure (10–20 atmospheres) converter. This recycle process, using cobalt catalysts, has been described above. In the same pilot-plant unit used for the recycle process work on a cobalt catalyst, the Lurgi Company developed similar processes using iron catalysts. This unit, which was installed at Hoesch-Benzin at Dortmund in 1938, consisted of a single tube of the standard middle-pressure reaction as built by Gutenhoffnungshutte. The annular layer of catalyst had an inside diameter of 24 mm., an outside diameter of 44 mm., and a depth of 5 meters. The tube was water-jacketed with a vapor chamber connected to the top by means of which the steam pressure could be controlled to give the desired synthesis temperature.

Dr. Herbert (Research Director of Lurgi) stated that the best iron catalyst developed by his laboratory has the following composition: 100 Fe, 25 Cu, 9 Al_2O_3 , 2 K_2O , 30 SiO_2 . The catalyst is prepared by dissolving copper and aluminum nitrates in a 10% solution of ferric nitrate in such quantities as will give the specified ratio of metals. The solution is heated to boiling, and a 10% solution of sodium carbonate is added rapidly at about 70° C. in the quantity required to precipitate the metals as hydroxides. The kieselguhr is then added rapidly, stirred for about 1 minute, and the mixture washed to a pH of 8.0, after which it is washed with a potassium carbonate solution to incorporate the specified quantity of K_2O . The product is dried in a centrifuge sufficiently to permit extrusion, and is dried further on a conveyor belt by a blast of hot air to facilitate cutting into desired lengths. Final drying is done at 106° C.

This catalyst is preferably reduced in the synthesis unit with hydrogen at 250–350° C. for 1–4 hours. The rate of hydrogen flow is 1 cubic meter/kg. catalyst/hour. Reduction with synthesis gas is possible. Synthesis is started at about 180° C., and the temperature is raised to 220° C. in 2 days. The operating pressure was 20 atmospheres. The space velocity (volumes of gas per volume of catalyst per hour) of fresh gas is 100, of recycle gas 300, and the tail-gas volume is 48% of the fresh-gas volume. Over an operating period of 3 months, the temperature is raised from 220 to 230° C. This catalyst has not been run to exhaustion by Lurgi, but it is believed that its life would be about 1 year. Other conditions of the operation and yields are shown in Table VI.

An iron catalyst which yields a higher proportion of gasoline in the product is made by impregnating Luxmasse with a solution of copper ammonium nitrate to obtain 3% by weight of metallic copper in the finished catalyst. The resulting catalyst is not highly active and requires a high operating temperature, but at this temperature it gives a relatively low boiling product, with less catalyst deterioration due to carbon deposition than would occur with a more active catalyst. The operating temperature

is 275° C. and pressure 20 atmospheres. The space velocity of fresh gas is 100, of recycle gas 300, and the tail gas volume is 50.5% of the fresh gas

TABLE VI
Lurgi Recycle Operation for High Wax Production

GAS COMPOSITION:	CO ₂	CO	H ₂	CH ₄	N ₂	CnHm
Fresh gas	5.8	37.6	48.1	0.1	8.4	0.0
Total feed gas	22.9	26.9	31.8	2.0	15.0	1.4
Tail gas	28.2	22.6	27.0	2.7	17.6	1.9
YIELDS, G./NORMAL CUBIC METER FROM TWO-STAGE OPERATION:						
Hard wax		66		Alcohols		9
Paraffin		22		Gasol (C ₃ +C ₄)		15 ^c
Oil		29 ^a		C ₁ +C ₂		22
Gasoline		29 ^b				

^a Olefins, 45%.

^b Olefins, 60%.

^c Olefins, 60%.

Total yield of liquid products plus gasol equals 170 g./normal cubic meter.

volume. Wax, oil, and gasoline are removed before recycling. The gas composition and yield and product distribution are shown in Table VII.

TABLE VII
Lurgi Recycle Operation for High Gasoline Production

GAS COMPOSITION:	CO ₂	CO	H ₂	CH ₄	N ₂	CnHm
Fresh gas	2.8	53.2	35.6	0.1	8.3	..
Total feed gas	31.8	29.8	19.8	3.5	14.0	1.3
Tail gas	48.0	16.7	11.3	5.3	16.5	2.2
YIELD G./NORMAL CUBIC METER FROM SINGLE-STAGE OPERATION:						
Paraffin		8		Alcohols		5
Oil		20 ^a		Gasol (C ₃ +C ₄)		32 ^c
Gasoline		70 ^b		C ₁ +C ₂		35

^a Olefin content, 60%.

^b Olefin content, 75%.

^c Olefin content, 70%.

Total yield of liquid products plus gasol equals 135 g./normal cubic meter.

In pilot plants identical with the Lurgi Company unit of the middle-pressure converter described above, simultaneous tests were run on six different iron catalysts (54).

Tables VIII, IX, and X contain the data on these comparative tests, conducted at the Braunkohle-Benzin A.G. in Schwartzheide-Ruhland. One catalyst was submitted by each of the following organizations: Kaiser

TABLE VIII
Catalysts Used in Cooperative Tests at Schwartzheide

Company	Copper (zinc)	K ₂ CO ₃	Carrier	Apparent density, g./cc.	Reduction (induction)
	Parts/100 parts of iron				
Kaiser Wilhelm Lurgi Brabag	1	0.75	None	1.02	2 H ₂ +1 CO, 325° C.
	10	9 K ₂ O from K ₂ SiO ₄	24 SiO ₂ from K ₄ SiO ₄	0.79	H ₂ , 30% Reduction
	10	0.5	None	1.37	Water gas, 245° C. (H ₂ or 2 H ₂ +1 CO, 225° C.)
	(10)				
I. G. Farbenindustrie ^a Ruhrchemie Rheinpreussen	..	1	None	2.27	H ₂ , 500° C. Complete reduction
	5	0.5 to 2	50 Kieselguhr	0.44	H ₂
	5	0.5 to 1	Powdered dolomite	0.68	H ₂ , 300-400° C. (Watergas, 245° C.)

^a Contained 2% (Al₂O₃+CaO).

Wilhelm Institute, Lurgi, Brabag, I. G. Farbenindustrie, Ruhrchemie, and Rheinpreussen.

Because the objective was to replace cobalt catalysts in existing plant, the highest permissible temperature in these tests was 225° C., and the

TABLE IX

Cooperative Tests on Iron Catalysts at Schwartzheide

(10 Atmospheres, 200–225° C. synthesis gas was 88% 1 CO + 1.25 H₂ and 12% inerts. Yields per cubic meter are based on feed gas. Space velocity is volumes (N.T.P.) of feed gas per volume of catalyst per hour.)

	Kaiser Wilhelm Institute	Lurgi	Brabag	I. G. Farben- industrie	Ruhr- chemie	Rhein- preussen
Space velocity	109	107	111	115	104	104
CO converted, %	85	88	77	81	70	62
CO:H ₂ , use ratio	0.80	0.66	0.69	0.74	0.72	1.07
Maximum yield, g./cubic meter	147	142	141	144	147	168
Average yield, g./cubic meter	125	124	108	117	103	104
Average yield, tons/day	3.26	3.19	2.88	3.23	2.57	2.60
Kg. C ₅ + /hr./m. ³	10.9	11.6	10.8	10.9	8.8	8.5

TABLE X

Cooperative Tests on Iron Catalysts at Schwartzheide

Product Distribution in Weight Per Cent

	Kaiser Wilhelm Institute	Lurgi	Brabag	I. G. Farben- industrie	Ruhr- chemie	Rhein- preussen
Wax	18.1	35.2	43.0	21.0	25.6	13.1
(Olefins)	(2)	(13)	(11)	(12)	(8)	(2)
Diesel, C ₁₁ to C ₁₈	14.2	13.2	16.3	11.2	12.8	13.5
(Olefins)	(15)	(39)	(47)	(45)	(23)	(19)
Gasoline, C ₅ to C ₁₀	25.0	19.4	17.6	25.4	22.2	29.6
	(48)	(51)	(67)	(59)	(44)	(48)
C ₃ +C ₄	19.8	12.2	10.6	18.6	14.5	21.5
(Olefins)	(53)	(66)	(76)	(71)	(62)	(53)
C ₂ H ₄	0.9	2.7	2.2	2.8	2.2	0.7
C ₂ H ₆	7.8	2.6	2.3	4.9	4.4	8.1
CH ₄	8.0	5.6	3.8	9.0	7.0	8.1
C ₁ +C ₂ +C ₃						
(Alcohols)	6.1	9.1	4.2	7.1	11.3	5.4

(Figures in parentheses are per cent of olefins in the fraction.)

operating pressure was 10 atmospheres of $1.25\text{H}_2 + 1\text{CO}$ gas (containing 12% inert gas). The analysis of the synthesis gas showed 6.2% CO_2 , 39.2% CO , 48.8% H_2 , 2.6% CH_4 , and 3.2% N_2 . The duration of the tests was 3 months. The temperature and space velocity were independently varied by each operator to secure optimum yields and durability. At the end of 2 weeks all units had reached about 200°C . The space velocities were in the range 105–110 volumes of synthesis gas per volume of catalyst per hour.

Only three of the six catalysts operated 90 days with one filling of catalyst. The others encountered "coking" difficulties and had to renew the charges repeatedly (four times in the case of Rheinpreussen). A description of the method of preparation of only one of the catalysts was found. The catalyst submitted by the Kaiser Wilhelm Institute was prepared in the following way: The iron was precipitated from the boiling dilute nitrate solution by the boiling soda solution. One per cent copper (based on the iron) had been added to the iron solution before precipitation. The precipitate was filtered and washed with hot distilled water until free from alkali. A paste was then made with distilled water and a solution of potassium carbonate (containing 1% of potassium carbonate, based on the iron) was mixed with the paste. The paste was thickened on a waterbath and drying completed at 105°C . in an oven. The dried pieces were then broken into granules of 2–4 mm.

The pretreatment of the catalyst was as follows: A mixed gas, rich in hydrogen ($2\text{H}_2 + 1\text{CO}$), was passed over the catalyst for 24 hours at a pressure of $1/10$ atmosphere and a temperature of 325°C ., (8 l. gas/hour/10 g. iron). The strongly pyrophoric catalyst was then soaked in paraffin wax to protect it from oxidation, and put into the converter with as little contact with air as possible.

At the beginning of the synthesis, the catalyst was very active at 185 – 190°C . To maintain a high conversion throughout the 3-month test, the temperature was raised gradually from 195 to 224°C ., most of the operation being conducted between 215 and 220°C .

The Ruhrchemie Fe:Cu:CaO:kieselguhr catalyst was probably prepared as follows: Calculated amounts of iron and copper turnings and calcium carbonate are dissolved in nitric acid, to yield a solution containing, in grams per liter, 115–125 g. iron, 5–7 g. copper, 11–13 g. calcium oxide, and no excess of nitric acid. The iron is in the ferrous state. Before precipitation, this solution is diluted with distilled water to lower the iron concentration to 36–55 g./l. This solution, heated to 98°C ., is run into a boiling solution of 90–100 g. soda ash/l., while being stirred vigorously. The quantity of soda ash used is such that, at the end of the precipitation, the pH is 6.8. Then 30 parts kieselguhr/100 parts iron are added to the mix-

ture. The total time of precipitation must not exceed 5 minutes. The mixture is filtered rapidly and washed with hot water until the filter cake contains 0.5% of sodium nitrate based on its content of iron. More complete washing is undesirable because of loss of calcium carbonate. About 200–220 cubic meters of wash water per ton of iron is sufficient.

After washing, the filter cake is repulped and enough potassium hydroxide added so that after a subsequent additional filtration 3.0–3.5 g. KOH/100 g. iron are retained. This is achieved if the concentration of KOH in the mother liquor is about 6 g./l. After impregnation, the suspension was filtered and the filter cake dried at 110° C. and subsequently crushed and screened. This procedure yields a catalyst containing Fe:Cu:CaO:kieselguhr in the proportions 10:5:10:30 parts by weight.

The I. G. Farbenindustrie catalyst was fused Fe_3O_4 containing 2% $\text{Al}_2\text{O}_3 + \text{CaO}$ and 1% K_2CO_3 . The Lurgi, Brabag, Ruhrchemie, and Rheinpreussen catalysts probably were precipitated from nitrate solutions. The presence of about 35% of calcium carbonate in the Rheinpreussen catalyst may have been responsible for the relatively rapid formation of carbon. The silica and kieselguhr in the Lurgi and Ruhrchemie catalysts also are known to decrease the durability of iron catalysts.

The CO to H_2 consumption ratios given in Table IX show that 50% or more of the oxygen appeared as water. This is much greater than the yield of water reported in laboratory tests by the Bureau of Mines and the Kaiser Wilhelm Institute. The yields of liquid products obtained from the Kaiser Wilhelm Institute and the Lurgi catalysts were only about 20% below those recorded for cobalt catalysts at 10 atmospheres. The highest wax yields (see Table X and Fig. 2) were obtained from the Lurgi and Brabag catalysts, whereas the Rheinpreussen catalyst had the lowest wax yield. The Diesel oil yield was lower than the gasoline yield for all of the catalysts. Despite a higher yield in grams per cubic meter of synthesis gas per pass through the converter, the space-time yields were about the same as those obtained in Bureau of Mines laboratory tests, using unpromoted iron catalysts precipitated from ferric nitrate solution with potassium carbonate (55).

In the United States, several oil companies have developed a fluidized iron catalyst process for producing motor gasoline by the Fischer-Tropsch process (56–64). In the pilot-plant work on this fluidized-iron process, doubly promoted synthetic ammonia catalyst, Fe_3O_4 , Al_2O_3 , and K_2O , 97, 2.5, and 0.5%, respectively, has been used. The fused catalyst is finely ground and completely reduced by hydrogen before use. It is then introduced while protected by an inert atmosphere, such as CO_2 or oxygen-free flue gas, into the converter. The pilot-plant converters are about 12-inches i.d. by 24-feet high, and contain an internal heat-exchange surface. This

heat exchanger consists of a bundle of about 12 1-inch closed-end tubes, each containing an inner tube through which water or Dowtherm is circulated at the pressure corresponding to the operating temperature. In an alternative design, the converter is jacketed and the internal heat-exchange tubes are connected to this jacket at the top and bottom of the converter.

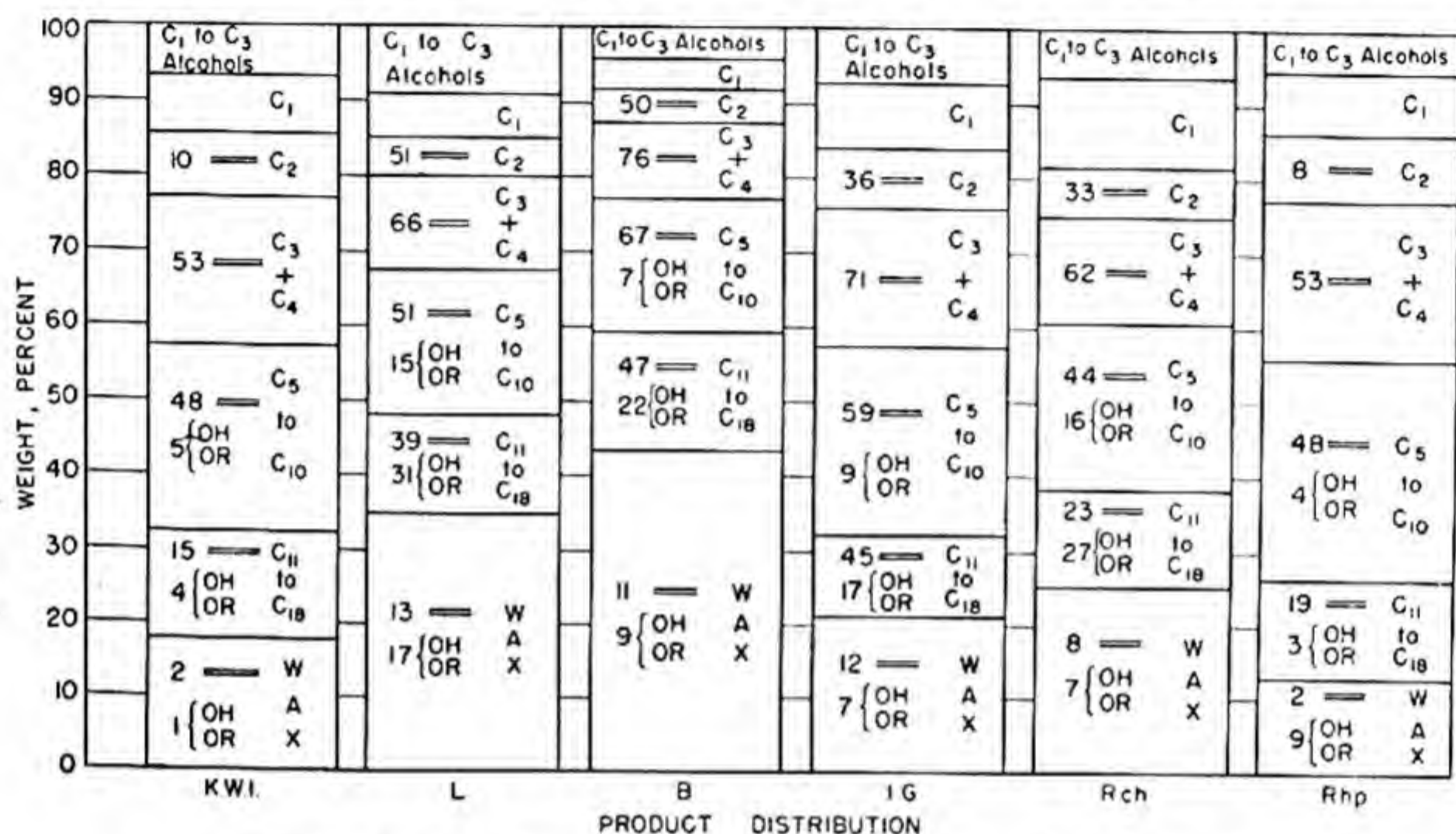


FIG. 2. Co-operative tests on iron catalysts at Schwartzheide.

== = Olefins, OH = Alcohols, OR = Esters, K.W.I. = Kaiser Wilhelm Institute, L = Lurgi, B = Brabag, I.G. = I.G. Farben, Rch = Ruhrchemie, Rhp = Rheinpreussen.

Pilot-plant operation is conducted usually at 300–325° C., 20-atmospheres pressure, with recycle of 3–4 volumes end gas/volume fresh feed. The latter is 1.8 to 2.0 H₂ to 1 CO, prepared by oxidation of natural gas with oxygen-steam mixtures at 300–400 p.s.i. and 1200° C. The synthesis operation is in “fixed” fluidized bed; that is, the bed of catalyst is suspended in the flowing gas with no “carry-over” of powdered catalyst outside the converter. Carry-over is completely avoided by the use of Aloxite filters in the expanded section of the top of the converter. Catalyst density in the fluidized bed is 60–80 pounds/cubic foot at the start. This density decreases during the first 2–14 days of operation to 10–20 pounds/cubic foot because of “spalling” of the catalyst induced by carbon formation. With a hydrogen-rich total feed gas, 1600 hours of continuous operation was achieved, and with a carbon dioxide-rich feed gas, only about 400 hours. Operation is limited to 1.5–2.5 linear feet/second gas velocity; at this velocity conversions of 90–95% are obtained per pass so that multistage opera-

tion is unnecessary. Carbon dioxide-rich feed gas operation results in a product which is chiefly highly olefinic gasoline with minor amounts of Diesel oil and oxygenated compounds (chiefly C_2 - C_5 alcohols, plus some aldehydes and ketones). Only a fraction of 1% wax is produced, but this is sufficient to occasionally cause defluidization of the bed. The gasoline, with only little refining, is a suitable motor fuel of about 75 motor octane number which can be appreciably increased by addition of polygasoline from the C_2 and C_3 olefins and by tetraethyl lead.

Based on this pilot-plant work, a plant of about 8000 barrels/day has been designed and is to be erected at Brownsville, Texas. Synthesis gas is to be made by reacting natural gas at about 400 p.s.i. with oxygen and

TABLE XI
Space-Time Yield of Various Fischer-Tropsch Processes

Catalyst	Temp., °C.	Pressure, atm.	C ₃ + ^a kg./m. ³ /hr.	Liquid product distribution			Water solubles organics	Steel ^b ton/bbl./day
				Gasoline	Diesel	Wax		
GRANULAR CATALYST, EXTERNALLY COOLED, NO GAS RECYCLE								
Co	175-200	1	8	56	33	11	V.S. ^c	2.7
Co	175-200	10	10	35	35	30	V.S. ^c	2.4
Fe	200-225	10	10	32	18	35	15	2.5
GRANULAR CATALYST, EXTERNALLY COOLED, GAS RECYCLE								
Co	190-224	10	13	50	22	22	6	1.9
Fe	230	20	14	19	19	56	6	2.1
Fe	275	20	14	68	19	8	5	2.2
POWDERED CATALYST — OIL SLURRY, GAS RECYCLE								
Fe	250-275	20	20	50	32	14	4	1.2
GRANULAR CATALYST, INTERNALLY COOLED, GAS RECYCLE								
Co	175-225	7	40	35	35	30	V.S. ^c	0.8
Fe	240-260	20	40	40	26	24	10	0.7
Fe	270-290	20	60	60	15	15	10	0.6
GRANULAR CATALYST, HOT-GAS RECYCLE								
Fe	300-320	20	32	70	17	1	12	0.7
FLUIDIZED CATALYST, GAS RECYCLE								
Fe	300-320	20	65	75	15	1	9	0.6
Co	175-240	3	30	61	38	1	V.S. ^c	0.8

^a Weight of total product excluding methane, ethane, and ethylene, per volume of catalyst per unit time.

^b In converter and its accessories only.

^c V.S. = very small.

steam in two vessels, each about 2000 cubic feet in volume. The synthesis converters reportedly will be six in number, and each of about 3500 cubic feet volume. They are to be fed with 350,000,000 cubic feet/day fresh synthesis gas and 750,000,000 cubic feet of recycle gas.

During the past two years, the Federal Bureau of Mines (65) has developed a process in which the heat of the reaction is removed from a granular or pelleted catalyst bed by the evaporation of an oil introduced along with the synthesis gas. The converter contains no metal heat-exchange surfaces, and the operation is essentially adiabatic. Temperature control is precise, and there is no radial temperature gradient. The vertical gradient is about 25° C. and is a thermodynamic consequence of the decrease in partial pressure of synthesis gas as the reaction proceeds. Most of the operations thus far have been with a cobalt-thoria-kieselguhr catalyst, for which a study was made of the change in space-time yield with space velocity of the $2\text{H}_2 + 1\text{CO}$ feed gas. Currently, a similar study is in progress with an iron catalyst. Further operations using recycle of end gas and two or more stages will be investigated to determine the maximum space-time yields.

The estimates of Table XI, except those in the first three rows, are based on very meager amounts of data and therefore are only preliminary approximations. As may be seen in Table XI, the internally cooled converter process, in its present (1947) stage of development, has a space-time yield about two-thirds of that of the fluidized iron catalyst process with about 30% more steel necessary for installing of the converter and its auxiliary equipment. The I.C.C. process is quite versatile in that various types of catalyst, and a variety of operating pressures may be used. The product distribution can be varied, therefore, over a wide range.

IV. PROCESSES RELATED TO THE FISCHER-TROPSCH SYNTHESIS

The "synol" process for the production of alcohols is identical with the Fischer-Tropsch synthesis using an iron catalyst, differing from it only in space velocity of feed gas and operating temperature (41). Passage of $1\text{CO} + 0.8\text{H}_2 + 20$ to 50 volumes of recycle gas, at 18 to 25 atmospheres and 190–200° C. over a catalyst which was a fused mixture of 97% Fe_3O_4 , 2.5% Al_2O_3 and 0.5% K_2O previously reduced at about 450° C. with hydrogen, yielded about 160 g./cubic meter of fresh gas of a mixture of hydrocarbons and alcohols. The boiling range and composition of the product are given in Table XII.

The catalyst was prepared by burning pure iron in oxygen to form a molten mass of oxide. Aluminum nitrate and potassium nitrate are then added to the melt and the fused mixture cooled and crushed to 1 to 3 mm. particle size. The finished preparation contained 97% Fe_3O_4 , 2.5% Al_2O_3 ,

0.2 to 0.6% K_2O , 0.16% sulfur, and 0.03% carbon. Its bulk density, after crushing, was about 2.0. This catalyst was reduced for 50 hours in pure dry hydrogen at about 450° C. About 2000 volumes hydrogen/hour are passed through 1 volume of catalyst at a linear velocity of at least 20 cm. second. The reduced catalyst is transferred in an atmosphere of carbon dioxide to the reactor.

TABLE XII

Composition of Synol Products

Boiling range, °C.	Per cent of total product	Per cent in fraction			
		Alcohol	Aldehydes	Fatty acids	Esters
34-105	29.7	20 ^a	4	0.2	2
105-150	19.7	55	6	0.7	2.5
150-175	5.0	44	8	0.3	4.5
175-218	12.7	55	4	0.3	8
218-255	9.2	55	2	0.4	10
255-290	6.4	49	3	0.5	15
290-320	5.5	45	3	0.5	19.5
320-360	4.8	35	4	0.6	20
over 360	2.1

^a Low, because of solubility in reaction aqueous phase.

Full-scale commercial development was not completed for the synol process. Twenty-five laboratory to pilot-plant size units were operated, ranging in size from 0.2-36 l. of catalyst, to study the relative merits of multistage vs. single-stage operation and gas recycle vs. single-pass operation. A four-stage unit of 100 l. catalyst capacity, producing 3-5 tons/month of liquid product was operated for 9 months. The catalyst was contained in 14-mm. i.d. tubes spaced 26 mm. from the center of any tube to the center of a neighboring one. The results of development work in this pilot plant indicated the following operating conditions for a two-stage process: *First stage*: Feed gas, 20-50 volumes recycle gas/volume fresh gas ($1CO:0.8H_2$); space velocity, 2500 to 5500 volumes total feed gas/volume catalyst/hour; temperature, 185° C. at start, 195° C. at end of 3 months, 225° C. at end of 9 months; pressure, 20 atmospheres. The gas and vapors from the converter would pass through a hot separator to remove wax, then through a cold separator to remove the alcohol and liquid hydrocarbons, and finally through a recycle gas heater back to the converter. A portion of the recycle gas would be sent to the *second stage*, which is identical with the first so far as flow diagram is concerned, except that recycle gas from the first stage is the "fresh-gas" for the second stage and that about one-third of the second-stage recycle gas is continuously purged by passage

from the cold separator through active charcoal and then into the fuel-gas mains. Conversion in the first stage is 65 and in the second 25% of the synthesis gas. To avoid corrosion, alkali must be added just beyond the hot-wax separators. Plugging of reactor tubes due to carbon deposition was the chief operating difficulty.

The synol process is of interest in a discussion of the Fischer-Tropsch reaction for the following reasons:

(1) The same catalyst, when used at a higher temperature as in the hot-gas recycle process, yields chiefly hydrocarbons, with only 5–10% alcohols, whereas in the synol process a very high recycle ratio of about 100 with drying of the gas on each cycle yields as much as 70% conversion to alcohols. The total conversion is over 90% to alcohols plus hydrocarbons, with only a very small amount of carbon dioxide produced. It is likely that the formation of the normal straight-chain alcohols, which constitute the bulk of the synol alcohol product, precedes the formation of olefins on this iron catalyst at 20 atmospheres in the temperature range 190–325° C.

(2) Carbon deposition apparently is proceeding at an appreciable velocity even at 190–225° C. under the conditions of the synol process. The formation of carbon at 300–325° C. in the hot-gas recycle or the fluidized iron catalyst processes, therefore, is not peculiar to the elevated temperatures used in those processes, although its rate is higher at the higher temperatures.

The "OXO" process consists in reacting olefins with carbon monoxide and hydrogen to produce aldehydes, and subsequent reduction of the aldehydes with hydrogen to alcohols. The basic reaction was discovered by the Ruhrchemie, and a large-scale continuous process resulted from co-operative effort of Ruhrchemie and I. G. Farbenindustrie (41, 66). A slurry of liquid olefin plus 3–5% reduced Fischer-Tropsch cobalt-thoria-magnesia-kieselguhr catalyst is pumped along with $1\text{H}_2 + 1\text{CO}$ gas (about 0.2 cubic meter/l. olefins) through a preheater (150–160° C.) into the reactors at 200-atmospheres pressure. The first reactor is 20-cm. i.d. by 8-meters high, it contains six 21-mm. o.d. by 17-mm. i.d. cooling tubes connected to a cooling jacket around the converter. The second reactor is in series with the first and contains some baffles but no cooling tubes, and an equal amount of gas (0.2 cubic meter/l. olefin) is pumped into the second reactor. The excess $\text{H}_2 + \text{CO}$ in both reactors serves to agitate the reaction mixture. Ethylene and propylene react readily when used in solution in a liquid medium. The contact time is about 20 minutes. Most of the catalyst is filtered off and recycled. The conversion is 70% in the first reactor and 30% in the second. The product consists of 80% aldehydes (about one-quarter of this is polymerized aldehyde) and 20% alcohols. It is not practical to isolate aldehydes from the first stage and it is considered prefer-

able to dehydrogenate the corresponding alcohols from the second stage (see below).

Because the hydrogenation of the aldehydes is retarded by carbon monoxide the first-stage product must be let down to atmospheric pressure. The second stage is operated with hydrogen at 170–195° C. and at 200-atmospheres pressure. Fischer-Tropsch cobalt catalyst or copper chromite may be used in the second stage. If the former is used, some carbon monoxide is formed by hydrogenation of cobalt carbonyl, and the exit gas is passed over an iron catalyst at 250° C. to convert the carbon monoxide to methane whose concentration, up to about 10%, is of only slight importance. The second stage is otherwise identical with the first. The first stage is not affected by sulfur compounds, but the second is quite sensitive; and if sulfur compounds are present, sulfide catalysts (such as a mixture of nickel and tungsten sulfides) must be used.

The reaction in the first stage probably is a homogeneous catalytic reaction, with either cobalt carbonyl or cobalt hydrocarbonyl as the catalyst. The insensitivity to sulfur poisoning, and the fact that any finely divided reactive cobalt compound may be used, agrees well with this assumption.

The aldehydes and alcohols produced are a mixture of normal and iso-compounds. This is due not only to the orientation of the hydrogen with respect to the C-CO bonds in the initial reaction complex but also to the isomerization of the olefin under the process conditions. It may be significant that nickel carbonyl does not readily shift the olefin double bond under the "OXO" process conditions, and nickel compounds are very poor catalysts for the process. From isooctene 32% *n*-nonyl alcohol, and from propylene 50% *n*-butyl alcohol are obtained, the remainder of the products being isoalcohols. In general, using α -olefins as raw material, one obtains about 60% isoalcohols. The synthesis will not occur unless a labile hydrogen atom is available in the olefin reactant. With diolefins the reaction takes place at only one double bond.

It is possible that a reaction similar to the "OXO" reaction occurs on the surface of catalysts during the synthesis of hydrocarbons and alcohols by the Fischer-Tropsch and the "synol" processes, and accounts for the small (about 10%) fraction of branched hydrocarbons and isoalcohols produced. In this connection it is of interest to note that as Pichler (37) indicated, the optimum operating pressures for nickel, cobalt, iron, and ruthenium Fischer-Tropsch catalysts increase in the order mentioned, and the difficulty of metal carbonyl formation also increases in this order.

The isoparaffin synthesis studied at the Kaiser Wilhelm Institut für Kohlenforschung (37, 67, 68, 69) is more closely related to the synthesis of the higher molecular weight alcohols using difficultly reducible oxides plus alkali as catalysts, than to the Fischer-Tropsch process. Thoria, zinc oxide,

alumina, or a mixture of these is the catalyst for the isoparaffin synthesis. The operating temperature is about 450° C. and pressure 300 atmospheres or higher of $1\text{CO} + 0.85\text{H}_2$. Figures 3 and 4 show the effect of operating

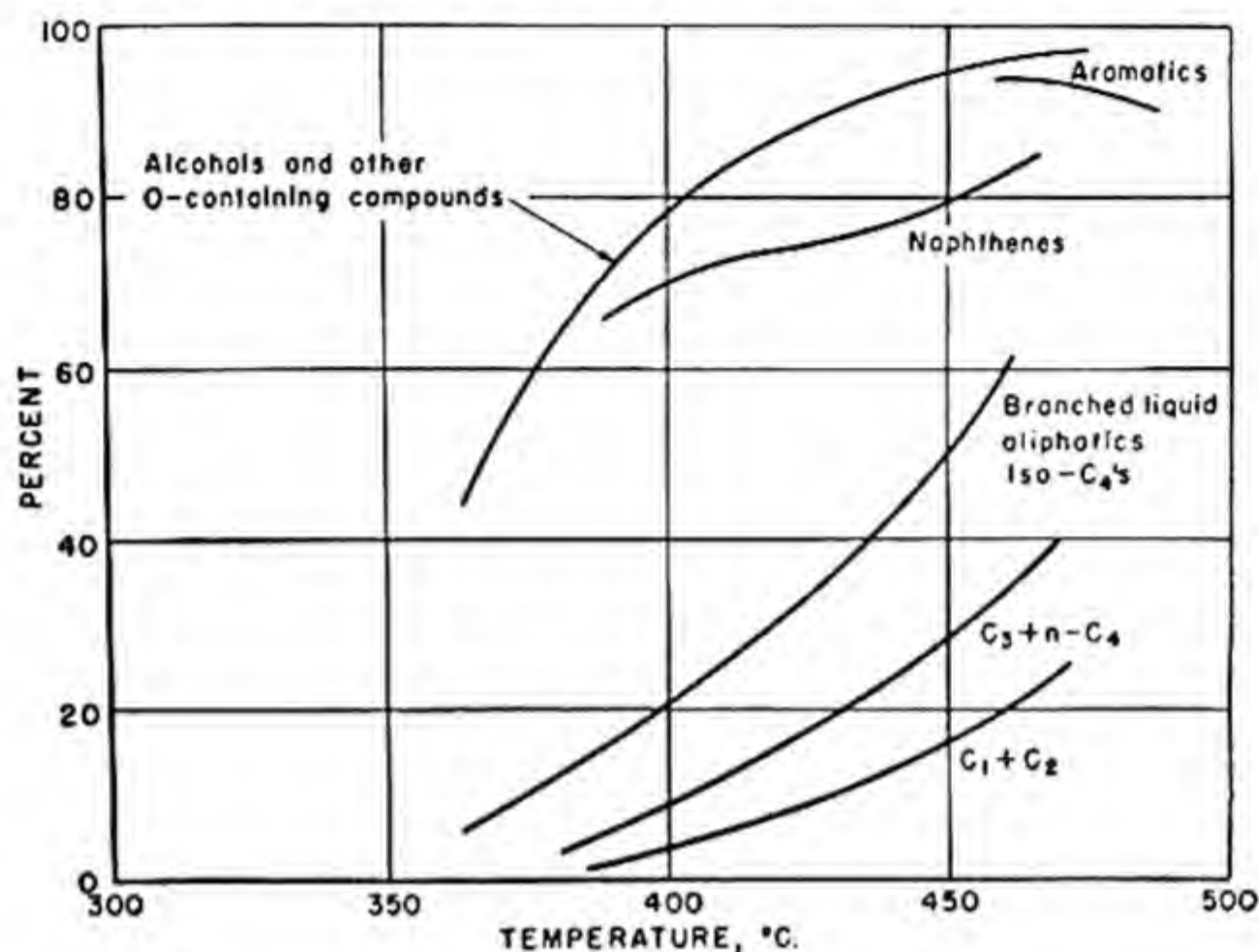


FIG. 3. Reaction product composition as related to temperature.
(ThO₂ single component catalysts)

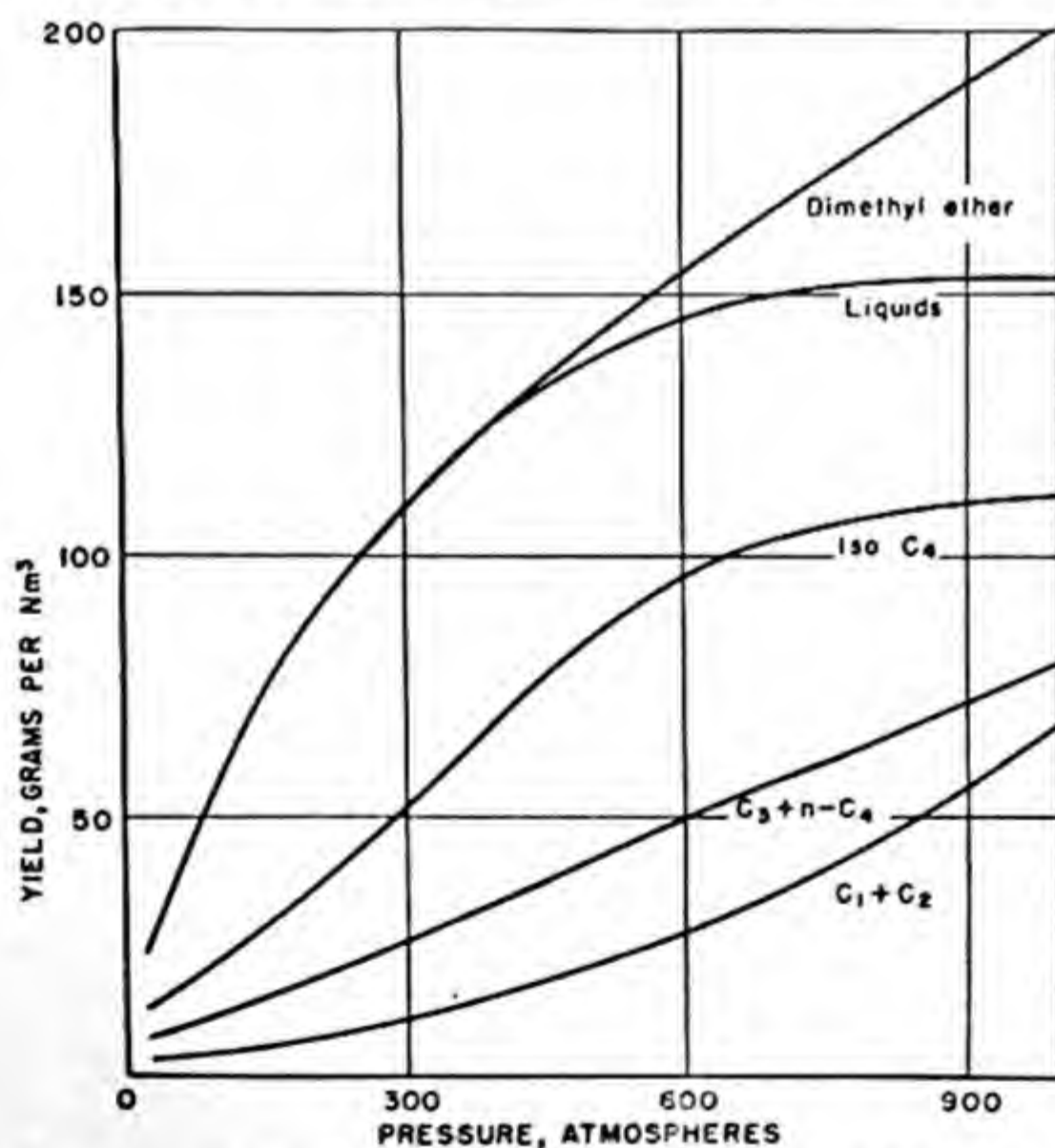


FIG. 4. Influence of pressure on the amount and kind of products
from the isosynthesis.
(ThO₂ single component catalysts, 450° C.)

temperature and pressure on the composition of the product using thoria as catalyst.

At 300 atmospheres and 400–450° C., using thoria plus 20% alumina and 3% potassium carbonate as catalyst and about 1000 volumes (measured at atmospheric pressure) of synthesis gas per volume of catalyst, 70% conversion per pass was obtained. The yield in g./cubic meter of synthesis gas was:

Liquid hydrocarbons	42
Iso-C ₄ hydrocarbons	51
<i>n</i> -C ₄ Hydrocarbons	7
C ₃ Hydrocarbons	18
C ₂ Hydrocarbons	6
CH ₄ Hydrocarbons	12
Water soluble alcohols	4
Oil soluble alcohols	2

The olefin and aromatic content of fractions of the liquid hydrocarbons increased with increasing boiling range of the fractions. Thus the 65–95° C. fraction contained 25% olefins, and no aromatics, and the 175–195° C. fraction contained 62% olefins and 31% aromatics.

After saturation of olefins and aromatics by catalytic high-pressure hydrogenation at low temperature, the liquid product contained 34% C₅, 21% C₆, 10% C₇, 5% C₈ paraffins, naphthenes, and 11% higher-boiling hydrocarbons. The C₅ fraction consisted of 91% 2-methylbutane and 9% *n*-pentane. The C₆ fraction contained 3% 2,2-dimethylbutane, 47% 2,3-dimethylbutane, 31% 2-methylpentane, 16% 3-methylpentane, and 3% methyleyclopentane; *n*-hexane was not detected.

V. CARBIDE FORMATION AND CARBON DEPOSITION ON IRON CATALYSTS

The formation of carbon on iron and iron-copper catalysts by the reaction $2\text{CO} = \text{CO}_2 + \text{C}$ has been studied by several investigators (70–73). The most significant result of this work (in so far as the Fischer-Tropsch synthesis is concerned) is the fact that neither an iron-free nor a copper-free carbon deposit was obtained. The data show that carbon is deposited in the crystal lattice of the catalyst and the inability to obtain a copper-free carbon deposit from tests with an iron-copper catalyst shows that iron carbonyl formation will not explain the results. It is very probable that carbon is formed from carbon monoxide by way of iron carbide as an intermediate. Carbide carbon diffuses rapidly throughout the crystal lattice and subsequently decomposes to yield elemental carbon, thus disrupting the lattice structure.

Pichler and Merkel (74) at the Kaiser Wilhelm Institut für Kohlen-

forschung showed that extensive conversion of iron catalysts to the carbide Fe_2C results in a highly active and durable Fischer-Tropsch catalyst. Thus, treatment with carbon monoxide at 1/10 atmosphere and 325°C . of precipitated iron catalysts yields a maximum of carbidic carbon of 4.6%, which corresponds to maximum activity and durability in the synthesis at 235°C . and 15 atmospheres pressure. The carbidic carbon content decreased to about 3.5% during the first few days of the synthesis but remained constant for months thereafter. The oxygen content of the catalyst was 0.6% at the start and increased to 1.6% at 112 days. In catalysts operated for long periods up to 550 days at 210 (start) to 285°C . (end temperature) the carbidic carbon dropped to 1%, the oxygen content increased to more than 20% and the elemental carbon to 8%. High $\text{H}_2:\text{CO}$ ratios in the feed gas reduce the rate of carbon formation. Alkalized iron catalysts form elemental carbon more rapidly than those containing little or no alkali.

Iron carbide (Fe_2C) of Curie point 265°C . is formed almost exclusively by treatment of precipitated, unreduced iron catalysts with 0.1 atmosphere of CO at 325°C . This carbide is only very slowly hydrogenated in pure hydrogen at $230\text{--}240^\circ\text{C}$. Promotion of precipitated catalysts speeds Fe_2C formation. There is some evidence for the existence of a carbide of Curie point 380°C ., which is obtained by treating a reduced (at 250°C .) iron catalyst with carbon monoxide at 220°C . A catalyst pretreated in this fashion is of low activity in the Fischer-Tropsch synthesis. Both carbides of Curie points 265 and 380°C . are converted to cementite (Fe_3C) upon heating at temperatures higher than 300°C . Precipitated iron catalysts which are not pretreated, but used directly in the synthesis at 235°C . and 15 atmospheres, show a slow increase in Fe_2C content. Thus after 120 hours the ratio $\text{Fe}_2\text{C}:\text{Fe}_3\text{O}_4$ is 3:10. The activity in the synthesis increases to a maximum during this period.

If one assumes that elemental carbon formation occurs by way of some form of iron carbide as an intermediate, the fact that increasing the $\text{H}_2:\text{CO}$ ratio in the synthesis gas reduces the rate of carbon formation may be explained in either of two ways:

(1) The hydrocarbon synthesis and the elemental carbon formation are competing for the available supply of carbide. Higher partial pressures of hydrogen are known to increase the rate of hydrocarbon synthesis and therefore the rate of elemental carbon formation would be expected to decrease with increase of $\text{H}_2:\text{CO}$ ratio. This explanation assumes that bulk carbide (as distinguished from surface carbide) is a necessary intermediate in the Fischer-Tropsch synthesis. As shown by the recent work of Emmett and his associates (75) using radioactive carbon as a tracer, this assumption is very probably incorrect.

(2) The formation of carbon to carbon bonds in the lattice of the catalyst must occur to obtain elemental carbon from metal carbide. If the diffusion of carbidic carbon to nuclei where such carbon to carbon bonding has started is retarded by the penetration of the lattice by atomic hydrogen, the rate of elemental carbon formation would decrease with increasing partial pressure of hydrogen. This explanation, based on rate of diffusion of carbidic carbon in the lattice, may serve also to account for the effect of alkali and other promoters or impurities. Thus the presence of alkali tends to preserve a structure similar to that of the spinels, and it is possible that carbidic carbon diffuses more readily through such a lattice than through that obtained when little or no alkali is present.

VI. KINETICS AND REACTION MECHANISMS IN THE FISCHER-TROPSCH SYNTHESIS

1. Pressure and Temperature Coefficients. Effect of Contact Time

The early work of Fischer and coworkers showed that pressures above 1 atmosphere favor the formation of oxygenated organic compounds and of high-molecular-weight hydrocarbons, and reduce the yield of normally liquid hydrocarbons per cubic meter of synthesis gas (76). Pressures lower than atmospheric necessitated proportionately greater amounts of catalysts for equal conversion to hydrocarbons, although the average molecular weight and chemical composition of the product were unaffected by the reduced pressure (77). In the absence of diluents, the reaction rate is approximately directly proportional to the pressure of $2\text{H}_2 + 1\text{CO}$ in the pressure range from 1 to 0.1 atmosphere.

TABLE XIII

Effect of Nitrogen Dilution on Yield

(Cobalt catalyst, atmospheric pressure, 100 volumes of $2\text{H}_2 + 1\text{CO}$ /volume of catalyst/hour)

Nitrogen, %	Yield, g. oil/m. ³	
	Observed	Calculated
1.0	101	...
16.3	88	84.5
28.8	90	72.3

On a cobalt catalyst at a total pressure of about 1 atmosphere, dilution with nitrogen does not decrease the percentage of conversion. In fact, such dilution results in a percentage of conversion somewhat greater than would

be calculated upon the basis of a first-order reaction. Storch and his co-workers (55) report the data in Table XIII on nitrogen dilution. Similar results have been reported by other investigators (78, 79).

The facts that in the absence of diluents the reaction is approximately first order and that in the presence of nitrogen the reaction rate is somewhat greater than corresponds to the partial pressure of the synthesis gas make it probable that the slow step in the reaction is the desorption of the products.

The retarding effect of the reaction products is illustrated by the data of Aicher, Myddleton, and Walker (80) who used a nickel catalyst: "If adsorption (of the products) is an important retarding influence on the reaction, the rate of reaction should vary directly as the partial pressure of reactants

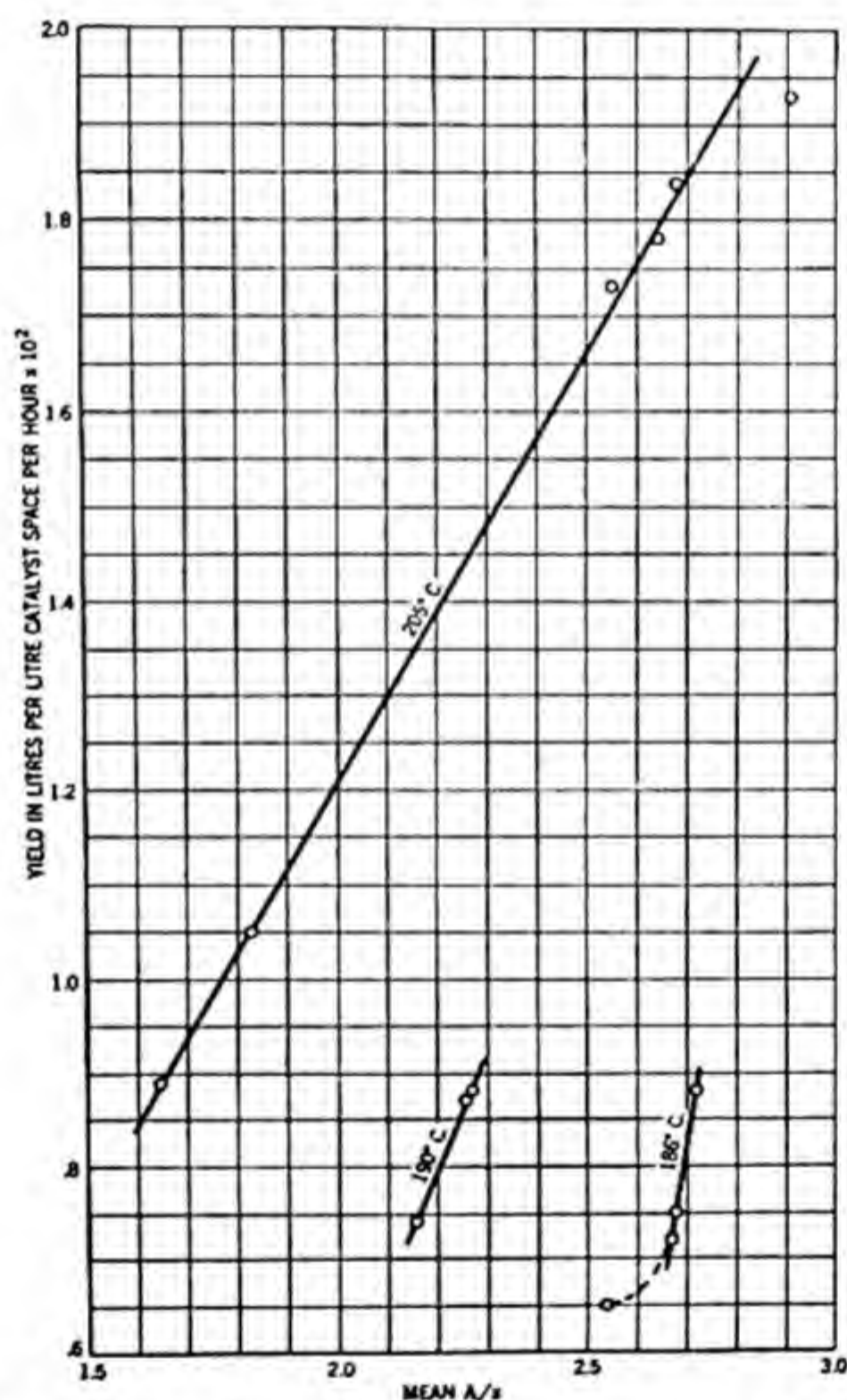


FIG. 5. Space-time yield as function of partial pressure, A , of reactants and partial pressure, x , of products; at 1 atmosphere total pressure.

and inversely as the partial pressure of the product. The yield of oil per unit time, per unit volume catalyst, would then bear a linear relationship to A/x , where A is the concentration of the reacting gas and x is the con-

centration of the product. By constructing graphs relating length of catalyst to yield, at various temperatures, and integrating these curves, we were able to estimate the average concentration of unchanged reactant in the experiments, over any catalyst layer."

Figure 5 is a reproduction of the data referred to in the quotation from Aicher *et al.* (80). The straight line for 205° C. fits the data reasonably well, and one may conclude that the rate is retarded by the adsorbed products of the reaction. The data for 190° C. (Fig. 5) are inadequate to determine a straight line, and those for 186° C. indicate that at low conversions there is some deviation from the rule of inverse proportionality to the partial pressure of the reactants. Some of the data of Aicher and coworkers (80) (Fig. 5) are suitable for calculating the temperature coefficient for relatively short contact times (that is, conversions of about 10–50%). The coefficient for the temperature ranges 197–207° C. and 191–207° C. are 1.4 and 1.67/10° C., respectively. These coefficients correspond to an activation energy per mole of about 20 kcal. as calculated from the Arrhenius equation. This energy value is reasonable for a desorption process.

Weller (81) studied the pressure dependence of the synthesis over a cobalt-thoria-kieselguhr catalyst, at about 1 atmosphere pressure using very short contact times so that the concentration of synthesis products was very low. Under these conditions the synthesis rate increased approximately as the square root of the synthesis gas pressure. The temperature coefficient in Weller's tests corresponded to an activation energy of 26 kcal./mole. Storch and his coworkers (55) obtained a value of 25 kcal./mole at long contact times corresponding to the Ruhrchemie process.

TABLE XIV
Effect of Pressures Above Atmospheric

Pressure, atm.	Yields, g./cubic meter synthesis gas				
	Total solid and liquid hydro- carbons	Paraffin wax	Oil boiling above 200° C.	Gasoline boiling below 200° C.	Gaseous hydro- carbons, C ₁ to C ₄
1.0	117	10	38	69	38
2.5	131	15	43	73	50
6.0	150	60	51	39	33
16.0	145	70	36	39	33
51.0	138	54	37	47	21
151.0	104	27	34	43	31

A study of the effect of pressures above atmospheric was made by Fischer and Pichler (82). As the pressure was increased above atmos-

pheric, the yield at first increased and then (at about 15 atmospheres) decreased. Table XIV shows the results of their work. A cobalt-thoria-kieselguhr catalyst and a constant throughput of 1 l. (measured at atmospheric pressure)/hour of $2\text{H}_2 + 1\text{CO}$ gas/ g. cobalt metal were used. The data are averages for 4-week operation. Only a single pass of the gas through the catalyst was made, and there was no catalyst regeneration.

Because of the constancy of throughput, the contact time increased in direct proportion to the pressure. The yield of all hydrocarbons (column 2 plus column 6) increased from 155 g./cubic meter at atmospheric pressure to 181 at 2.5 and 183 at 6 atmospheres, and then decreased with further pressure increase.

As the theoretical yield was about 208 g./cubic meter, the maximum percentage of conversion to hydrocarbons was 88–89. The rapid decrease in yield of hydrocarbons for pressures above about 16 atmospheres was probably due to corrosion of active catalyst surface by carbonyl formation and by the stronger adsorption of the oxygenated organic compounds which were produced in larger amounts at the higher pressures.

Martin's curves (32), illustrating the effect of pressure, are reproduced in Fig. 6 for comparison with data on the effect of pressure on a ruthenium catalyst by Pichler and Buffleb (83) at pressures from

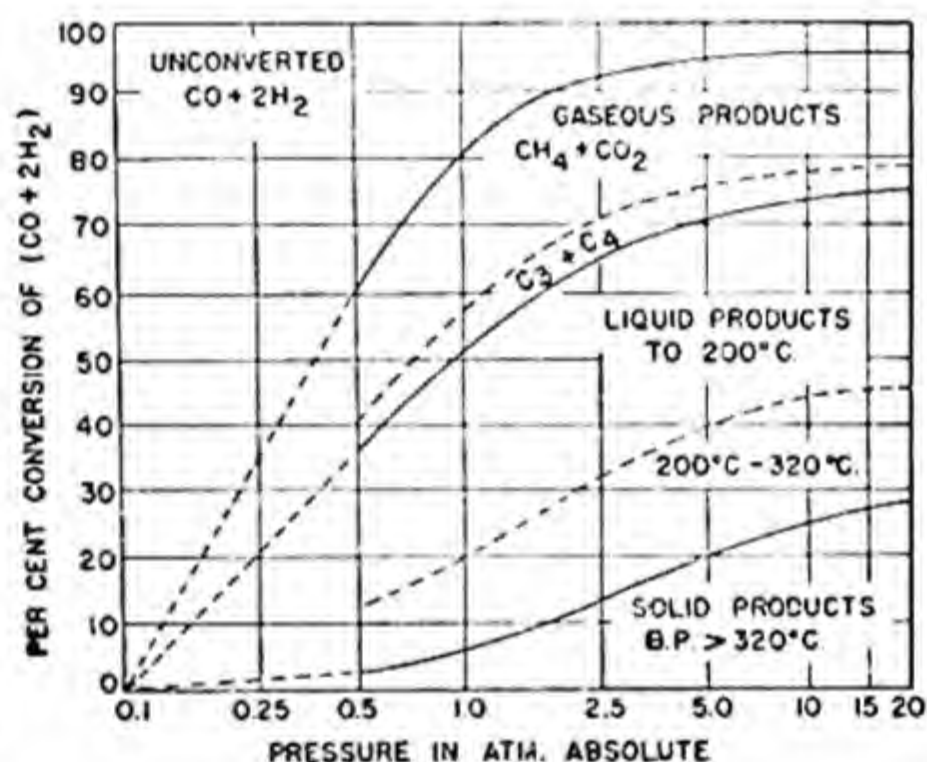


FIG. 6. Effect of pressure on total yield and yield of various fractions.

15 to 1000 atmospheres. The results of the latter work are shown in Fig. 7. Three grams of ruthenium catalyst was used, and the flow of synthesis gas was so adjusted that 1 l. (measured at 1-atmosphere pressure) of effluent gas was obtained per hour. The throughputs of $2\text{H}_2 + 1\text{CO}$ (calculated from the nitrogen contents of the ingoing and effluent gases) were 1.08, 1.16, 1.79, 2.57, 5.0, and 5.26 l./hour/3 g. ruthenium for 15, 30, 50, 100, 180, and 1000 atmospheres, respectively. It must be remembered that the data of Fig. 6 were obtained at a constant throughput per gram of catalyst, whereas those of Fig. 7 were measured at varying throughput. If the throughput had been kept constant at, for example, 1 l./hour/g. ruthenium, then the yield and conversions would have been appreciably lower at 15, 30, and 50 atmospheres, only slightly lower at 100 atmospheres, and slightly higher at 180 and 1000 atmospheres. Therefore, the curves of Fig. 7 on a constant throughput basis would have been steeper between 15 and 180 atmospheres. With

this in mind, a comparison of Figs. 6 and 7 shows that, for a cobalt catalyst, about 95% conversion is reached at 15 atmospheres, whereas for a ruthenium catalyst 95% conversion necessitates a pressure of about 300 atmospheres.

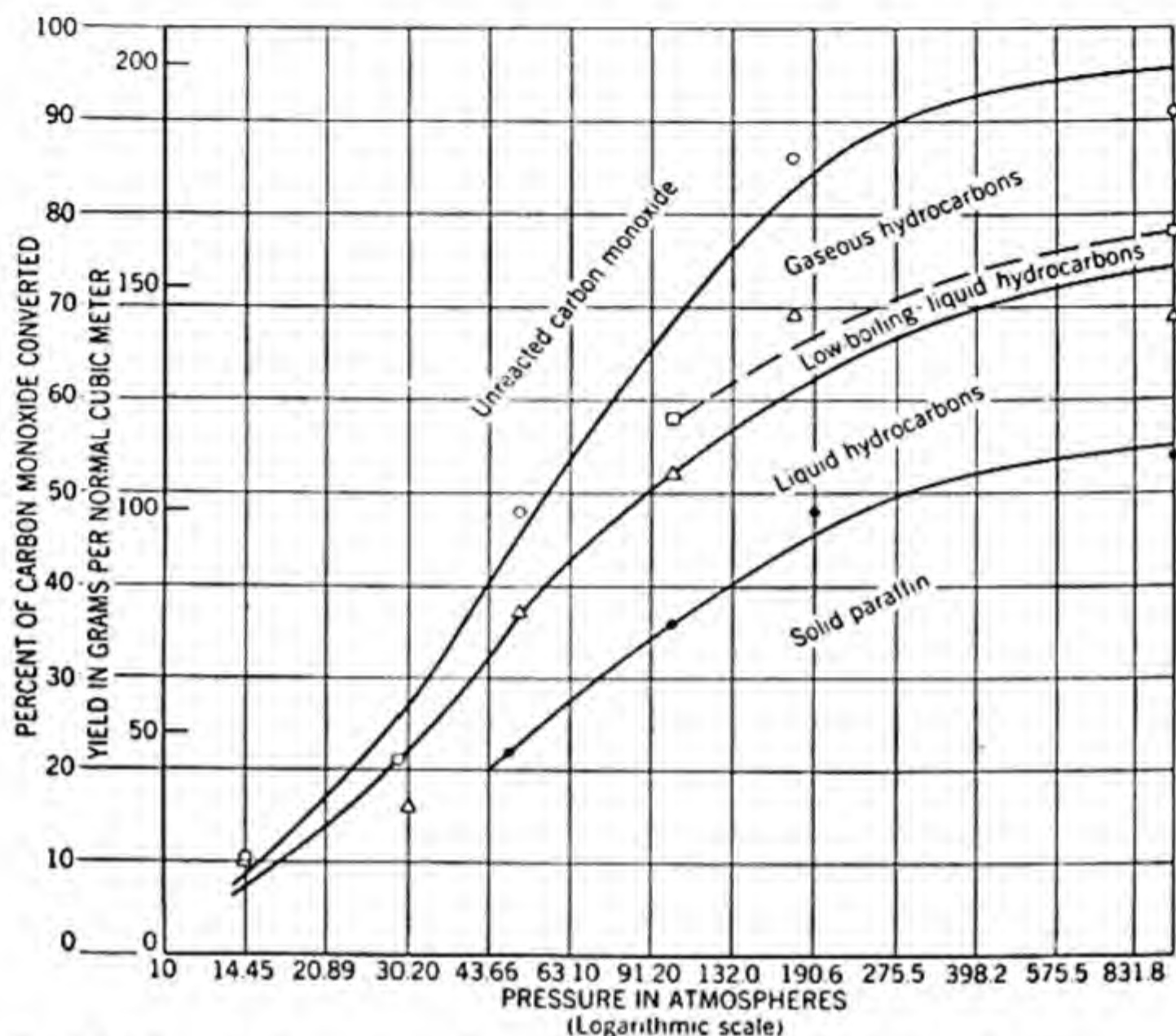


FIG. 7. Yield and character of products at 180° C. and various pressures.

It is interesting to note also that, whereas for a cobalt catalyst maximum life was obtained at 5–15 atmospheres pressure, only a few weeks of operation at 50–150 atmospheres sufficed to cause a large decrease in catalyst activity; for a ruthenium catalyst 6 months of operation at 100–1000 atmospheres did not result in any observable decrease in activity.

The effect of increasing space velocity at pressures above atmospheric is demonstrated by the data of Table XV calculated from the results of Fischer and Pichler's work (82).

The space-time yield (column 5) reaches a maximum at about 4 l./hour/g. cobalt. In column 6 the space-time yield was calculated as indicated in the footnote. The volume change upon reaction to form chiefly hydrocarbons with 5 to 16 carbon atoms is approximately constant over a wide range of variation of molecular weight distribution; therefore the partial pressure of the reaction products is approximately directly proportional to the contraction. The figures in column 6 increase more slowly than those of column 5 with increasing throughput, but there is no maximum. It seems probable that the temperature of the catalyst surface increases

with increasing throughput, despite the apparent constancy of the average temperature. At the higher temperatures a large proportion of the carbon monoxide used appears as gaseous hydrocarbons and as carbon dioxide.

TABLE XV

Effect of Varying the Throughput at 15-Atmospheres Pressure and 200° C., using 4 g. Cobalt (in Cobalt-Thoria-Kieselguhr)

1 2 H ₂ + 1 CO L./hr. at 1 atm.	2 L./hr./g. Co	3 Contraction, %	4 G./m. ³	5 Yield of oil (excluding gasol)		6
				G./1000 hr./g. Co (col. 4 × 2)	G./1000 hr./g. Co, calcd. from contraction ^a	
4.6	1.15	74	101	106		106
9.0	2.25	60	85	192		131
14.5	3.6	48	60	216		164
40.5	10.0	16	16.5	165		490

^a Assuming that the volume change upon reaction is constant for all throughputs and that yield is independent of the partial pressure of reactants and inversely proportional to partial pressure of products. Thus, taking 106 g./1000 hours as the basis for comparison, the second-row figure of column 6 is obtained from $106 \times 0.74/0.6$, the third row from $106 \times 0.74/0.48$, and the fourth from $106 \times 0.74/0.16$

Additional data on the effect of varying space velocity in the range of 0.24 to 2.16 l. 2H₂+1CO/g. cobalt, operating at 10-atmospheres pressure and using a cobalt-thoria-kieselguhr catalyst, are given by Fischer and

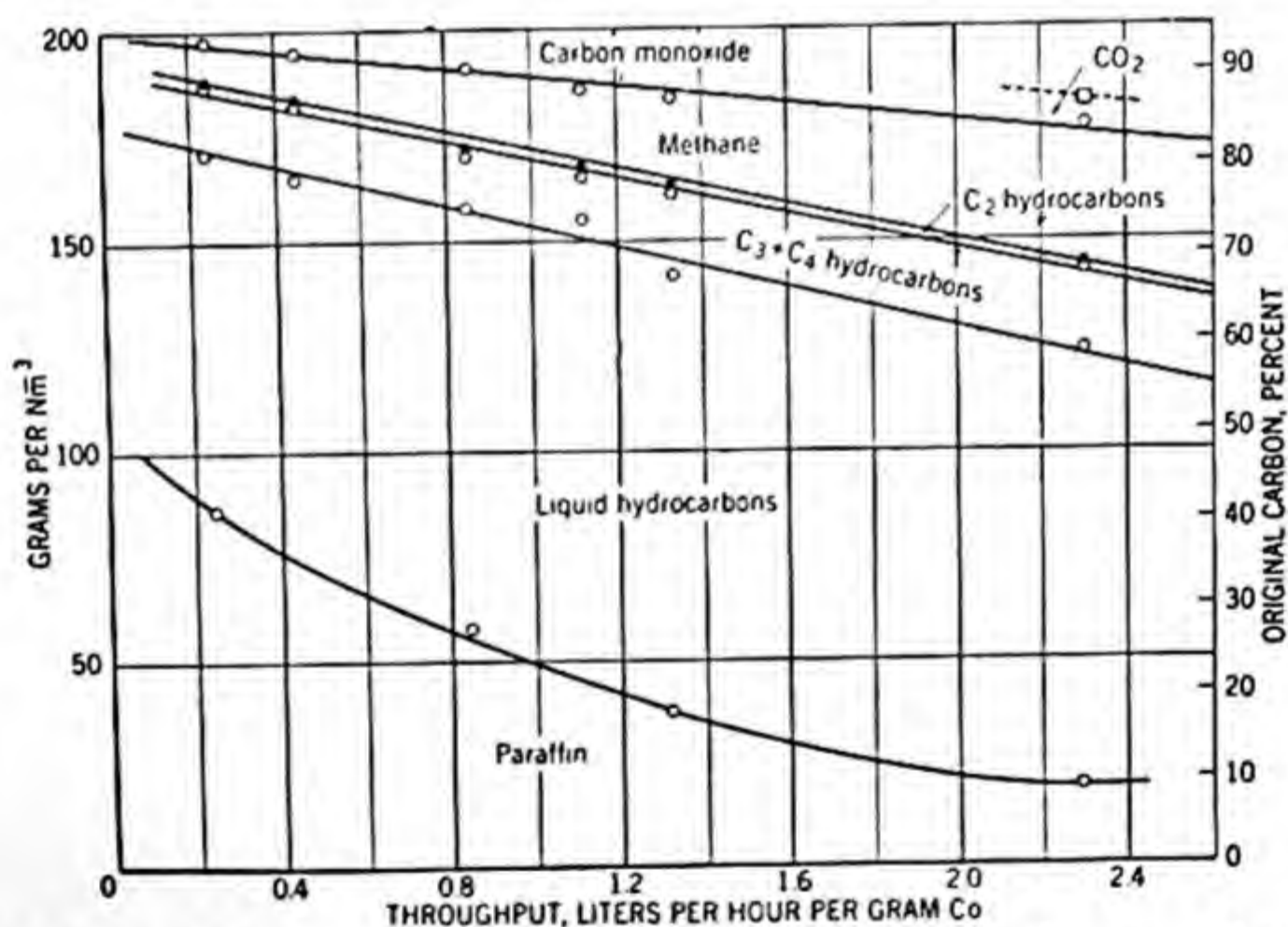


FIG. 8. Intermediate pressure synthesis yields and carbon balance vs. throughput.

Pichler (84). In each of these experiments the operating temperature was adjusted to obtain a minimum of methane and maximum of liquid plus solid hydrocarbons. The results are presented in Fig. 8, where the out-

standing fact is the extraordinarily small amounts of C_2 hydrocarbon produced. This marked discontinuity in the quantitative composition of the product is of interest in connection with the data given in an earlier section of this paper concerning the unique position of C_2H_4 in the synthesis on cobalt catalysts. Figure 8 shows that the yield of solid paraffin decreased with increasing space velocity, as did also the total yield of hydrocarbons other than methane. Because the data of Fig. 8 were obtained by separation of the condensable (at room temperatures and 10-atmospheres pressure) hydrocarbons in two stages, and because only the total amount of condensed hydrocarbons for both stages is given, it is not possible to correlate partial pressure of the products with space-time yield.

The effect of varying space velocity over a ruthenium catalyst at $230^\circ C.$ and 100-atmospheres pressure as given by Pichler and Buffleb (85) is presented in Table XVI. The space-time yield shows a maximum

TABLE XVI
*Effect of Space Velocity on a Ruthenium Catalyst
at $230^\circ C.$ and 100-atmospheres pressure*

1	2	3	4	5	6	7	8
L ^a ,/hr./ g. Ru	Contraction, %	Yield, g. liquid per			CO Converted to condensed hydrocarbons		Total hydro- carbons, g./l. catalyst space/hr.
		Cubic meter 2 H ₂ +1 CO	G. Ru/hr. ×100	L. catalyst space/hr.	Per cent CO used	Per cent CO reacted	
1.8	81	136	24	108	78	87	124
3.2	79	125	40	180	72	83	217
4.3	69	98	43	194	56	74	262
7.0	62	84	59	265	48	70	379
9.1	56	79	72	324	45	73	445
10.7	50	65	69	310	37	68	456
16.7	36	37	60	270	21	54	500

^a Measured at 1-atmosphere pressure.

at a throughput of about 9 l. $2H_2+1CO$ /hour/g. of ruthenium. The space-time yield (column 5) is plotted against the percentage of contraction (column 2) in Fig. 9. It was noted in column 5 of Table XV for a cobalt catalyst at 15 atmospheres that the space-time yield goes through a maximum at about 50% contraction. In Fig. 9 a similar maximum at about 55% contraction is observed for ruthenium at 100-atmospheres pressure. Apparently the heat transfer capacity of the apparatus used was exceeded as the throughput was increased. The resulting rise in temperature of part of the catalyst bed led to an increased space-time yield of gaseous hydrocarbons and a correspondingly lower yield of liquid hydrocarbons. Column

7 of Table XVI shows that, with increasing space velocity, the fraction of the reacting carbon monoxide which yielded condensed hydrocarbons decreased. As only negligible quantities of carbon dioxide are obtained (85) virtually all of the carbon monoxide which reacted yielded hydrocarbons. From columns 5 and 7 of Table XVI may be calculated the approximate

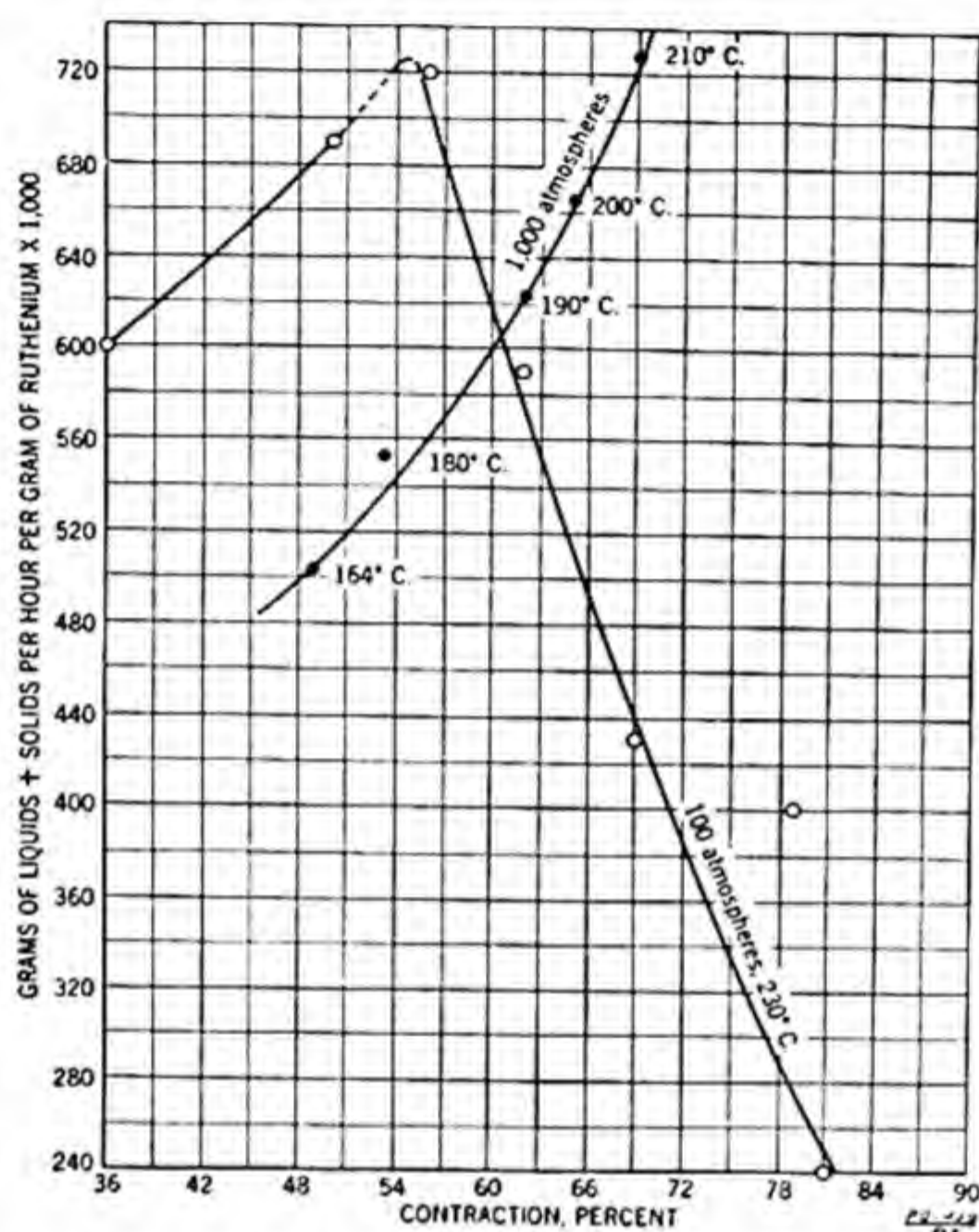


FIG. 9. Synthesis on ruthenium. Relation of space-time yield to contraction.

space-time yield of all hydrocarbons (solid, liquid, and gaseous). The results of such calculations (column 8) show no maximum yield such as is observed in column 5 and Fig. 9 for the yield of condensed hydrocarbons.

Pichler and Buffleb (85) also published some data on the contractions and yield obtained at several temperatures from a ruthenium catalyst at a constant space velocity of 7 l. $2\text{H}_2 + 1\text{CO}$ /g. ruthenium and at the higher pressure of 1000 atmospheres. These data are given in Table XVII.

The space-time yield of condensed hydrocarbons is plotted against contraction in Fig. 9. Within the limits of heat-transfer capacity of the apparatus, the yield is directly proportional to the contraction when the temperature is varied, because the temperature coefficient of the reaction rate apparently is large enough to overcome the increased retarding effect of the products with increasing conversion.

The effect of pressures above 1 atmosphere on the durability of a cobalt catalyst was investigated by Fischer and Pichler (82). Their results are presented graphically in Fig. 10. The pressures given are gage readings, so that the 0-atmosphere curve shows the results at 1-atmosphere pressure.

TABLE XVII

Effect of Temperature on Yield for Ruthenium Catalyst at 1000 Atmospheres

Temp. °C.	Contraction, %	Yield of liquid and solid hydrocarbons, g./m. ³	CO Converted to condensed hydrocarbons, per cent CO used
164	49	72	41
180	55	79	44
190	62	89	51
200	65	95	55
210	69	104	60

The yield of solid plus liquid hydrocarbons showed a minimum decrease with time for reaction pressures of 6–16 atmospheres. At these pressures the initial yield was more than 150 g./cubic meter, and after 26 weeks of operation the yield was still above 100 g./cubic meter. At 1-atmosphere pressure the yield dropped from 130 to 100 g./cubic meter in only 4 weeks of operation. At 151 atmospheres the decrease in yield with time was very rapid. At such pressures there was a noticeable formation of cobalt carbonyl and consequent corrosion of the catalyst surface.

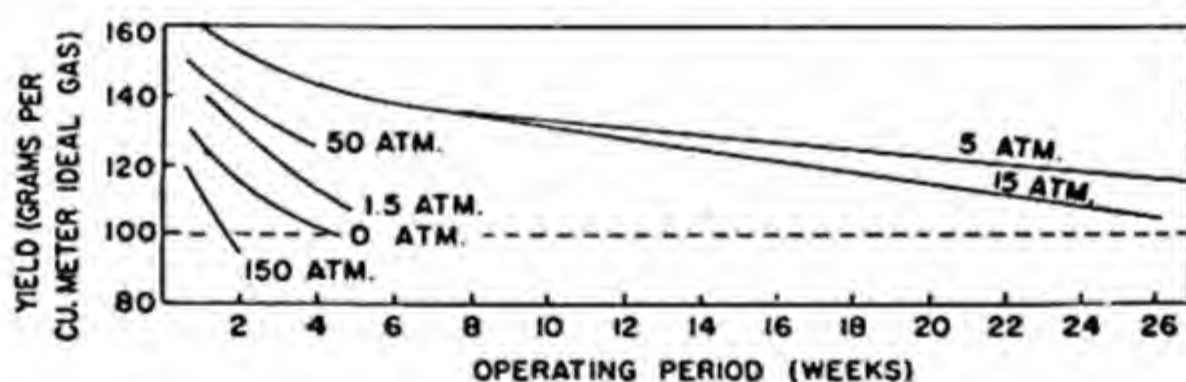


FIG 10. Variation of yield with time at various pressures.

The slower decrease in activity of the catalyst at medium pressures was shown also by the smaller temperature increase necessary to obtain the maximum yield of liquid and solid hydrocarbons. Increasing time of operation was associated with gradual lowering of the activity of the catalyst. This reduction could be partly compensated by raising the reaction temperature. In the experiments at 6–16 atmospheres the initial temperatures of 175–180° C. were not raised to 195° C. even after 6 months of operation. At 1 atmosphere the initial temperature of 180° had to be increased to 195° C. after only 5 weeks of operation.

Similar data on the effect of pressure on the durability of iron catalysts are presented by Pichler (37, 74, 86). Iron catalysts usually are much less durable at atmospheric pressure than are cobalt catalysts. As with the cobalt catalyst it is possible, however, by frequent flushings with hydrogen to keep a carefully prepared and pretreated iron catalyst active at atmospheric pressure for 6–12 months (37). The pressure coefficient of the synthesis on iron catalysts is shown in Fig. 11, prepared by Pichler (37) from

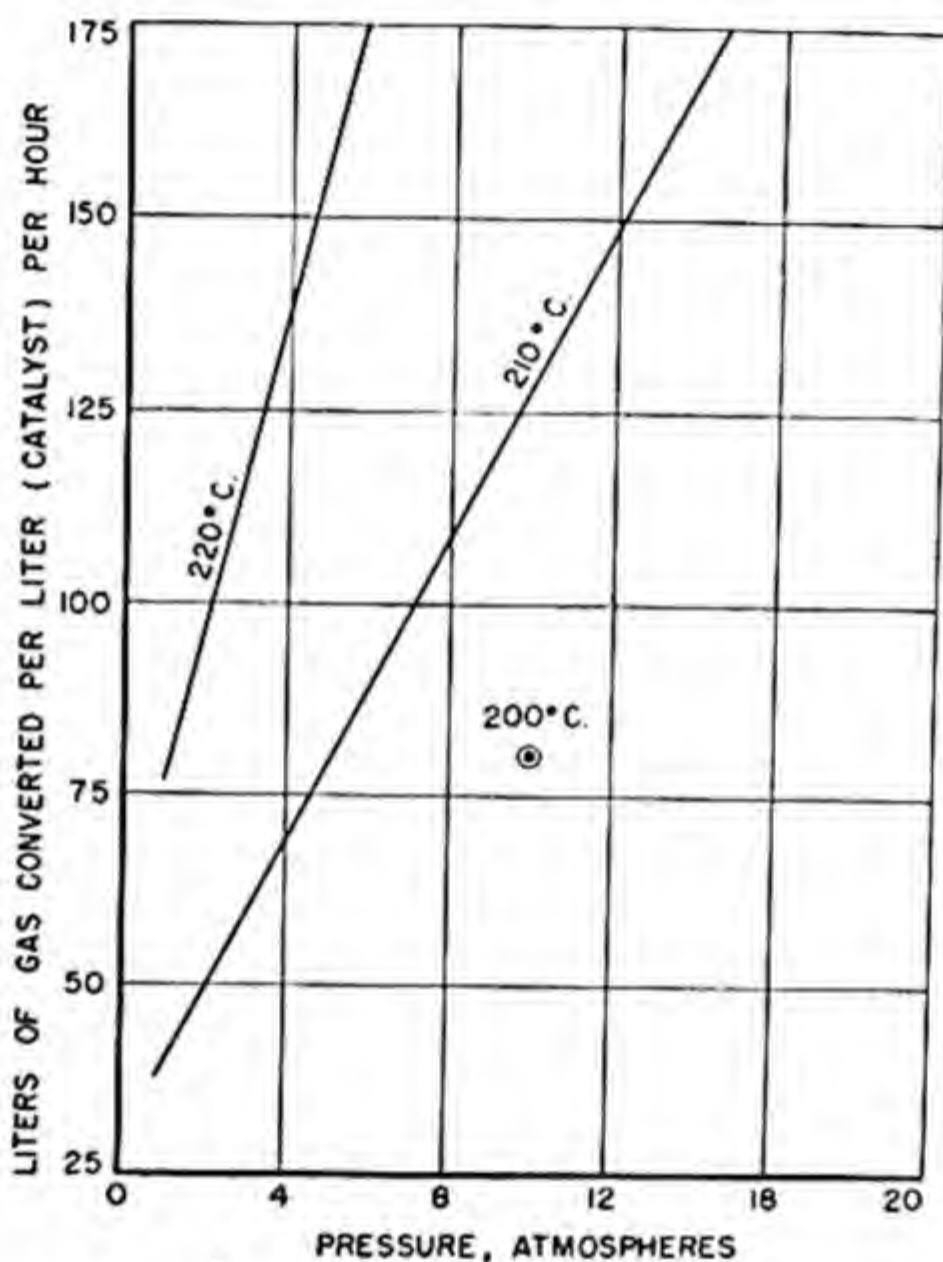


Fig. 11. Gas conversion on an active iron catalyst at various pressures. Extensive carbonyl formation above 20 atmospheres.

data obtained at the Kaiser Wilhelm Institut für Kohlenforschung. This pressure coefficient decreases with decreasing operating temperature and at about 175° C. probably would be close to that of a zero order reaction as found for cobalt catalysts.

2. Mechanism of the Synthesis

F. Fischer's hypothesis concerning the mechanism of the synthesis postulated the intermediary formation of cobalt or iron carbide and reduction of the carbide to methylene (CH_2) groups. The latter would subsequently polymerize to yield unsaturated paraffin hydrocarbons. Although direct hydrogenation of preformed cobalt or iron carbide yields largely

methane, with only minor amounts of other hydrocarbons, the hypothesis of Fischer could be correct because of the selective poisoning action of carbon monoxide and of the products of the synthesis in retarding the methane-forming reaction.

One of the earliest significant observations relating to the mechanism of the reaction was made in 1930 by Dr. D. F. Smith and his coworkers (16). They found that when ethylene was added to synthesis gas ($2\text{H}_2 + 1\text{CO}$) and the mixture passed over a Co-MnO-Cu catalyst at about 200°C ., the ethylene entered into the synthesis thereby increasing the yield of oil and of particularly of oxygenated organic compounds. When, however, an Fe-Cu catalyst was used, the oil yield was virtually unaffected by the presence of ethylene in the synthesis gas. This observation was directly confirmed by Craxford (17) in 1939. Dr. C. C. Hall of the British Fuel Research Laboratory (87) finds that when adsorbed wax on a cobalt catalyst is removed by treatment with hydrogen at about 210°C . the chain-length distribution curve for the products has the same peculiar form as the corresponding curve for the synthesis products. Thus, there is a minimum at C_2 for both synthesis and wax hydrocracking, a maximum at C_5 to C_6 for the synthesis products, and at C_8 to C_9 for the cracking products followed by an asymptotic approach to zero at higher molecular weights. This suggests to Hall the hypothesis that during synthesis, the array of interacting CH_2 groups on the catalyst surface may be regarded as a giant molecule and that observed synthesis products are fragments split off this by the attack of chemisorbed hydrogen atoms. When the surface concentration of the latter is low, little cracking will occur, and long chains will be produced; and as it increases more and more cracking will occur, the products will become shorter and shorter in chain-length, and finally only methane will be produced. Data on secondary reactions such as hydrocarbon cracking and the water-gas shift occurring on cobalt catalysts have been published by Craxford (88).

The concept of metal carbide as a synthesis intermediate has been used rather loosely. Distinction has rarely been made between bulk carbide and "surface" carbide as a possible intermediate. Craxford and Rideal (89), for example, speak of "surface" carbide; they give, however, as evidence for the carbide theory only examples which indicate that under some conditions bulk carbide accumulates in the catalyst. "Surface" carbide is very difficult to distinguish from an adsorbed reaction complex of hydrogen and carbon monoxide. Weller, Hofer, and Anderson (90) present evidence that bulk carbide, in the case of cobalt catalysts, probably is neither an intermediate in the synthesis nor a catalytically active substrate for the synthesis. They show that presence of extensive amounts of carbide in cobalt catalysts severely inhibits the Fischer-Tropsch synthesis. In one experiment, for example, a cobalt-thoria-magnesia-kieselguhr (100:6:12:200)

catalyst was reduced with hydrogen at 400° C. and carbided with carbon monoxide for 20 hours at 200° C.; the amount of carbon monoxide reacted was equivalent to 70% conversion of the cobalt to Co_2C . Exposure of this carbided sample to circulating synthesis gas resulted in an overall synthesis rate at 150° C. of $60\text{--}70 \times 10^{-4}$ g. carbon/g. cobalt/hour. After removal of the carbide by hydrogenation at 150–194° C. and re-exposure of the sample to synthesis gas, a synthesis rate of $250\text{--}300 \times 10^{-4}$ g. carbon/g. cobalt/hour was observed, an increase of 400%. It may be noted that the distribution of synthesis products was about the same in both cases.

In another case, a sample of cobalt-thoria-kieselguhr (100:18:100) catalyst which had been completely carbided at 210° C. was found to exhibit no appreciable activity in the synthesis under conditions where a control sample, similarly reduced initially but not carbided, gave copious yields of oil and water. Partial hydrogenation of the carbided sample at 190° C., with the removal of 72% of the carbon which had been introduced, restored the activity to about one-half the normal value.

It was further shown that the loss of synthesis activity on carbiding can persist even when synthesis is continued for several days. Another sample of cobalt-thoria-kieselguhr catalyst was carbided for 24 hours at 200° C. after initial reduction. On exposure to flowing synthesis gas at 180° C., the carbided sample originally showed no catalytic activity, as measured by the fractional decrease in gas volume (contraction) as the gas passed through the converter. During operation for 1 day at 180° C., the contraction rose to 20%, but it did not increase further during another day of synthesis. Increasing the temperature to 190° C. increased the contraction only to 32% even after a period of a day. Subsequent hydrogenation of the sample at 210° C. and re-exposure to synthesis gas resulted in a normal contraction of 60% at 180° C. Recarbiding of the active catalyst for 24 hours at 200° C. again reduced the activity to the low value observed after the first carbiding, and rehydrogenation of the carbided sample again restored the normal activity.

It should be noted that this inhibitory effect of precarbiding before synthesis is not explainable as a poisoning due to free carbon deposited during the carbiding, because the effect is completely reversed by hydrogenation at temperatures where free carbon is not affected. These experiments show that bulk cobalt carbide is not a catalyst for the synthesis; this conclusion, furthermore, is contrary to that which would be expected if bulk carbide were an intermediate in the synthesis.

Further evidence which indicates that bulk cobalt carbide is not of importance in the synthesis is furnished by x-ray analysis of catalysts which have been used in the synthesis. It has been shown (91) that on low-temperature carburization with carbon monoxide, reduced cobalt

catalysts form a carbide, Co_2C , which has a characteristic x-ray diffraction pattern. This fact provides a means of identifying cobalt carbide in the catalyst. It was then observed by x-ray analysis that if catalyst samples were partly carbided before synthesis and then used in synthesis, carbide was still present in the samples even after several days of synthesis. (In pure hydrogen, the carbide would have been completely removed as methane in several hours.) On the other hand, if the samples were used in the synthesis immediately after reduction (that is, no precarbiding), no carbide was ever found at the conclusion of the synthesis. In other words, bulk carbide is apparently not built up in appreciable quantity during steady-state synthesis, while carbide already present is apparently not removed at an appreciable rate during steady-state synthesis. Although quantitative determinations of the amount of carbide present under given conditions have yet to be made, the indication is that bulk carbide is neither formed nor destroyed as part of the synthesis process.

The final evidence to be adduced in connection with the role of bulk carbide is also based on x-ray analysis. It was shown (90) that cobalt in catalysts reduced at $360\text{--}400^\circ\text{C}$. is present primarily as cubic cobalt. Cubic cobalt is thermodynamically unstable with respect to hexagonal cobalt at temperatures below about 360°C . Carbiding of the reduced sample and hydrogenation of the carbide, both at 200°C ., always converts the cobalt to the low-temperature stable, hexagonal form. Now all samples of cobalt catalysts (not precarbided) which have been examined after use in the synthesis have given a diffraction pattern identical with that of the freshly reduced catalyst. If any appreciable amount of the cobalt had been through the cycle of carbiding and hydrogenation at any time during the synthesis, it would have appeared as hexagonal, not cubic, cobalt in the used catalyst sample. Since this did not occur, it follows that, within the limits of the x-ray method, the cobalt was not converted to bulk carbide and subsequently hydrogenated during the synthesis; that is, bulk carbide is not an intermediate in the synthesis.

Experiments have recently been completed by Kummer, DeWitt, and Emmett (75), using C^{14} as a tracer in the synthesis on an iron catalyst. The results are inconclusive. If the total catalyst surface is uniformly active in the synthesis, the results show that only a small fraction of the reaction proceeds by way of the carbide. However, if only occasional active patches of the surface are participating in the synthesis, then it is possible to interpret the results as indicating that all of the reaction proceeds by way of the carbide. The carbide intermediate hypothesis for the mechanism of the synthesis on iron catalysts, however, is probably incorrect. Thus, the results of recycle operations at low temperatures on iron catalysts show that alcohols are formed earlier in the synthesis than olefinic hydrocarbons.

This fact is particularly difficult to explain by the carbide-methylene polymerization hypothesis. It appears probable that the olefins are produced by dehydration of the alcohols and that the latter are very early products of the synthesis.

The fact that only a relatively small fraction of singly-branched hydrocarbons is produced in the synthesis on iron and cobalt catalysts is very difficult to explain on the basis of the carbide-methylene polymerization hypothesis. Branching should occur whenever a carbidic carbon is included in a methylene polymerization chain, and as there is according to this hypothesis a considerable supply of carbidic carbon, branching should occur much more often than is the case. Furthermore, there is no explanation offered by this hypothesis as to why the branch is limited to a single methyl group.

If alcohols are the precursors of the hydrocarbons in the synthesis, it is probable that a reaction analogous to the "OXO" synthesis occurs on the surface of Fischer-Tropsch catalysts. Such a reaction would account for the relatively small fraction of branched hydrocarbons and for the fact that the branches are almost entirely single methyl groups.

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The Catalytic Activation of Hydrogen

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I. INTRODUCTION

The mechanism of the catalytic activation of hydrogen gas and of hydrogen in organic compounds is of importance for numerous industrial processes, and for the problem of biological oxidation. In addition, there is the quite general problem of the relation between catalyst constitution and

catalytic activity and the hydrogen molecule, because of its simplicity, forms a very suitable substrate for investigations of this kind. The successive discoveries of atomic hydrogen, parahydrogen, and deuterium have given a great impetus to studies of catalysis, and the present article does not attempt to review all the work in this field. We shall stress mainly the work of Rideal and his school at Cambridge University, the results of other schools being treated in less detail.

The adsorption investigations of the late J. K. Roberts, using brilliant new techniques, has led to the view that many gases are chemisorbed by *clean* metal surfaces at room temperature in a rapid and irreversible fashion. The chemisorbed layer of hydrogen on tungsten, for example, only starts to evaporate into a good vacuum at 500° C., and for oxygen the temperature is much higher. This work, together with kinetic investigations of certain catalytic reactions (particularly the parahydrogen conversion and the exchange reaction between deuterium and ethylene) led Rideal (1) and his collaborators to the view that a catalytic reaction may occur between one gas adsorbed in a primary chemisorbed layer on the catalyst, and a second gas adsorbed above it, either in a true van der Waals' layer or at gaps in the chemisorbed layer. Rideal has summarized his contributions in his Sabatier lecture to the Society of Chemical Industry (2). This view is a distinct development in the theory of catalysis, and may be distinguished clearly from the Langmuir-Hinshelwood picture (3), in which two reacting gases compete for the chemisorbed layer, reaction occurring between two adjacent atoms or radicals. This latter picture, requiring, as it does, a close balance of two free energies of chemisorption, is indeed unlikely at low temperatures. In advancing this new picture of catalysis, the intention is to supplement rather than supplant the old picture, which is probably valid for many systems, particularly at relatively high temperatures. A decision between the two mechanisms may in certain cases be based on a measurement of heats of chemisorption, where the chemisorption concerned is relevant to the catalysis. In the present author's opinion this is only likely to be so for "clean" plane metal surfaces, where there is good reason to believe that the larger part of the surface is catalytically active. Until the details of adsorption and catalysis have been worked out on such surfaces, the interpretation of results on more complicated catalysts, such as promoted oxides, is bound to involve an element of uncertainty.

II. EXPERIMENTAL STUDIES OF CHEMISORBED HYDROGEN ON METALS

1. Methods

J. K. Roberts (4, 5) initiated important work in this field. In his first method the chemisorbed film was detected by its effect on the accommoda-

tion coefficient of the metal. In his second method the heat evolved on adsorption of the gas was measured. R. C. L. Bosworth and E. K. Rideal (6, 7) detected the adsorbed film by its effect on the electrical contact potential of the metal. In all these studies a tungsten wire was employed, because its high melting point allows it to be heated *in vacuo* to temperatures of 2500°K. , when all surface contamination is removed. The surface of the wire may be taken as a roughness factor ρ times its geometrical area, where ρ may be between 1 and 2. It has also been found possible to prepare clean tungsten surfaces of much larger area, e.g., 400 cm.^2 by evaporation from a wire (8). This method has the advantage that larger volumes of gas are adsorbed, but the disadvantage that the true area cannot be obtained

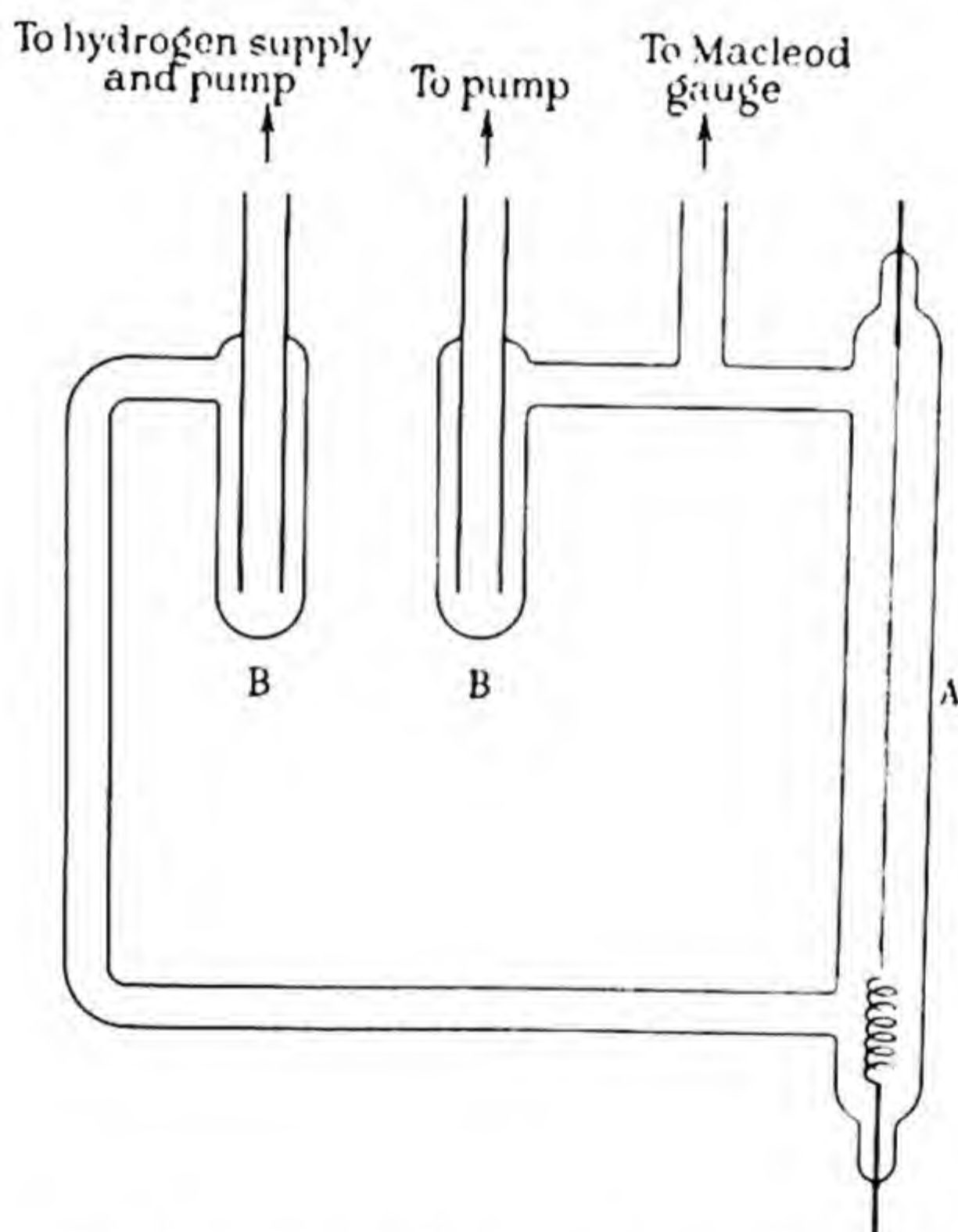


FIG. 1. Measurement of accommodation coefficients.*

from the geometrical area. The method has also been used to obtain clean surfaces of other metals, such as nickel, with areas of $10,000\text{ cm.}^2$ (9).

* Figures 1, 2, 3, 4, 7, and 8 are reproduced from J. K. Roberts "Some Problems in Adsorption," Cambridge University Press, London, 1939. Grateful acknowledgment is recorded to the author and publisher concerned.

2. The Accommodation Coefficient Method (4)

Neon gas at 0.1-mm. mercury pressure was circulated over a tungsten wire 18 cm. \times 0.0066 cm. sealed in tube A. Charcoal traps B cooled in liquid air protected the wire from oxygen, and a liquid air trap was inserted between the wire and the McLeod gauge. A standard current could be passed through the wire, raising its temperature about 20° above that of a bath surrounding A. The resistance of the wire, and hence its temperature T_2 , was determined by a Wheatstone bridge. An additional circuit allowed the wire to be "flashed" for a short time at 2500° K. to remove adsorbed films.

After circulating neon for some time, the wire was flashed and then switched over to the standard current, values of the wire resistance being taken at intervals of time from zero time (the time at which the flashing current was switched off). If T_1 be the temperature of the gas in tube A, q , the heat loss from the wire in cal. cm.⁻² sec.⁻¹, is given by Knudsen's equation,

$$q = 1.74 \times 10^{-4} \frac{ap}{\sqrt{MT_1}} (T_2 - T_1)$$

where a is the accommodation coefficient, M the molecular weight, and p the pressure in dynes cm.⁻². of the neon. Fig. 2 shows a plot of a against

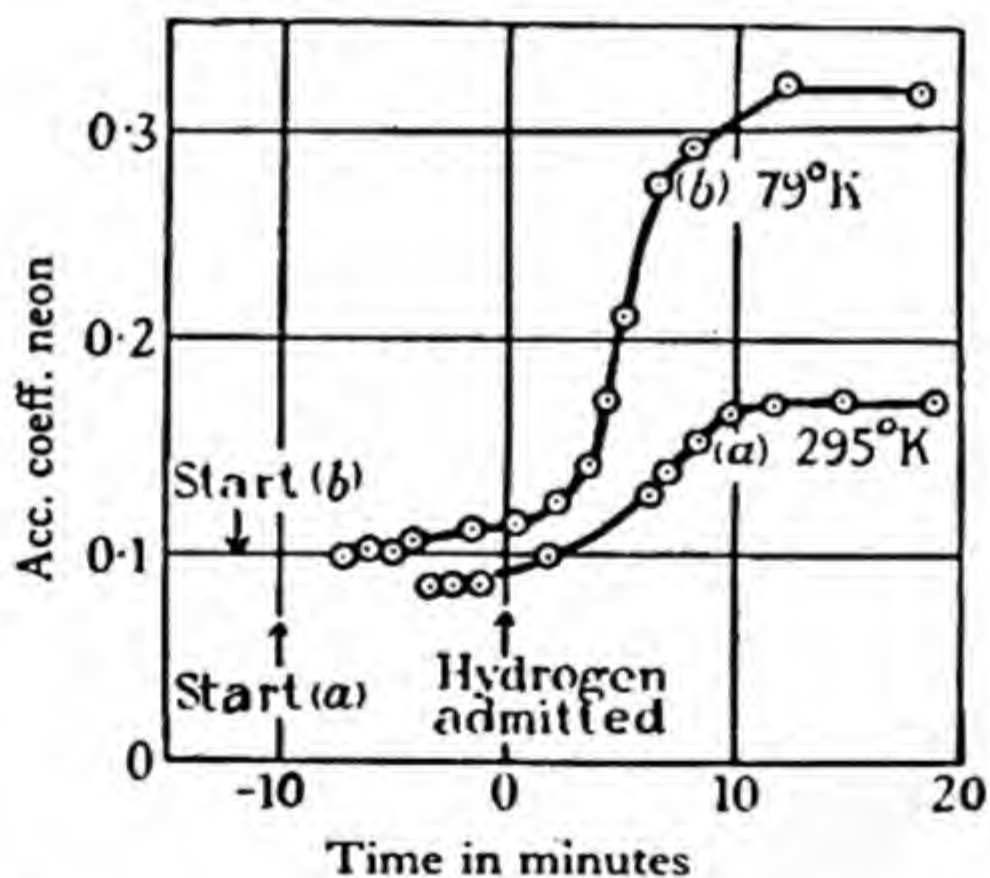


FIG. 2. Effect of adsorbed hydrogen on the accommodation coefficient. The arrow marks the time at which the flashing current was cut off.

time, showing a very slight drift due to adsorption of traces of impurity. Extrapolation back to zero time gives a value of a characteristic of the clean metal surface.

A trace of hydrogen was now admitted to the wire via the charcoal trap, sufficient to give a pressure of 4×10^{-4} mm. mercury. An immediate rise in a was found, a steady value being reached which was the same even if a ten times larger dose of hydrogen was admitted. It seems clear that a complete monolayer of hydrogen has formed on the wire, the adsorption process being rapid even at 79°K . A trace of admitted air was completely taken up by the charcoal traps and the effect observed was therefore not due to impurities in the hydrogen. A similar method has been used to detect oxygen films, and it was possible to distinguish three distinct types of film in this case (4, 10, 11).

3. Heat of Adsorption Method (4)

The apparatus comprised a tube, containing a fine tungsten wire, to which was attached a pirani gage calibrated for hydrogen, and a gas pipette. As before, the apparatus was pumped to a hard vacuum and the wire flashed

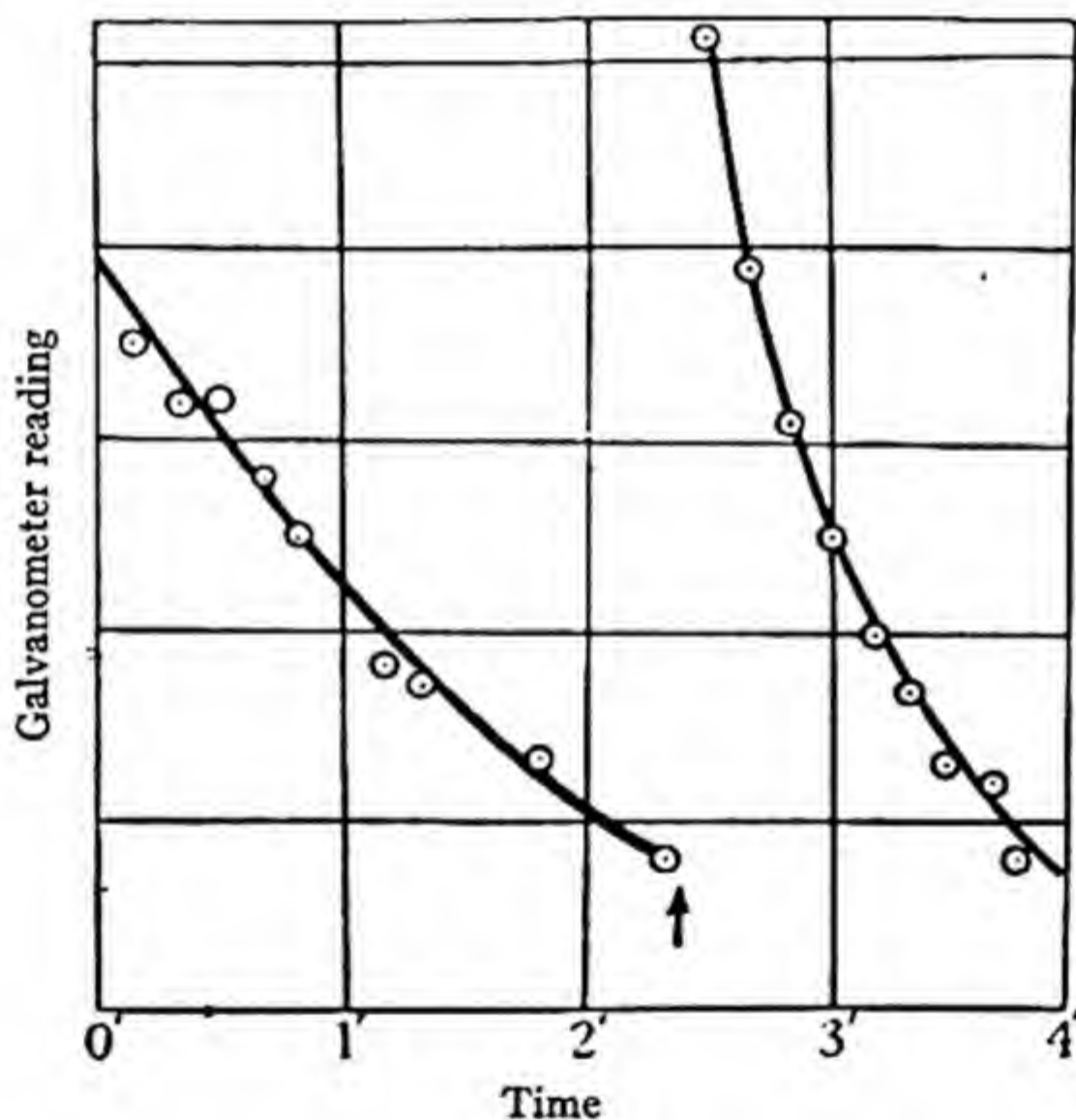


FIG. 3. A plot of the resistance of the wire (galvanometer reading) against time. The arrow indicates the time at which hydrogen was admitted.

As the flashing current was cut off, the wire was switched into a sensitive Wheatstone bridge in which a Paschen galvanometer was used. The decrease of the wire resistance with time as the wire cooled down is shown in Fig. 3.

On admission of a charge of hydrogen to the wire from the pipette the wire temperature rose abruptly. Successive charges were admitted until the pirani gage indicated the appearance of hydrogen in the gas phase, and thus the saturation of the adsorbed film on the tungsten. A wire of superficial area 0.55 cm.^2 was found to chemisorb 4.4×10^{14} molecules.

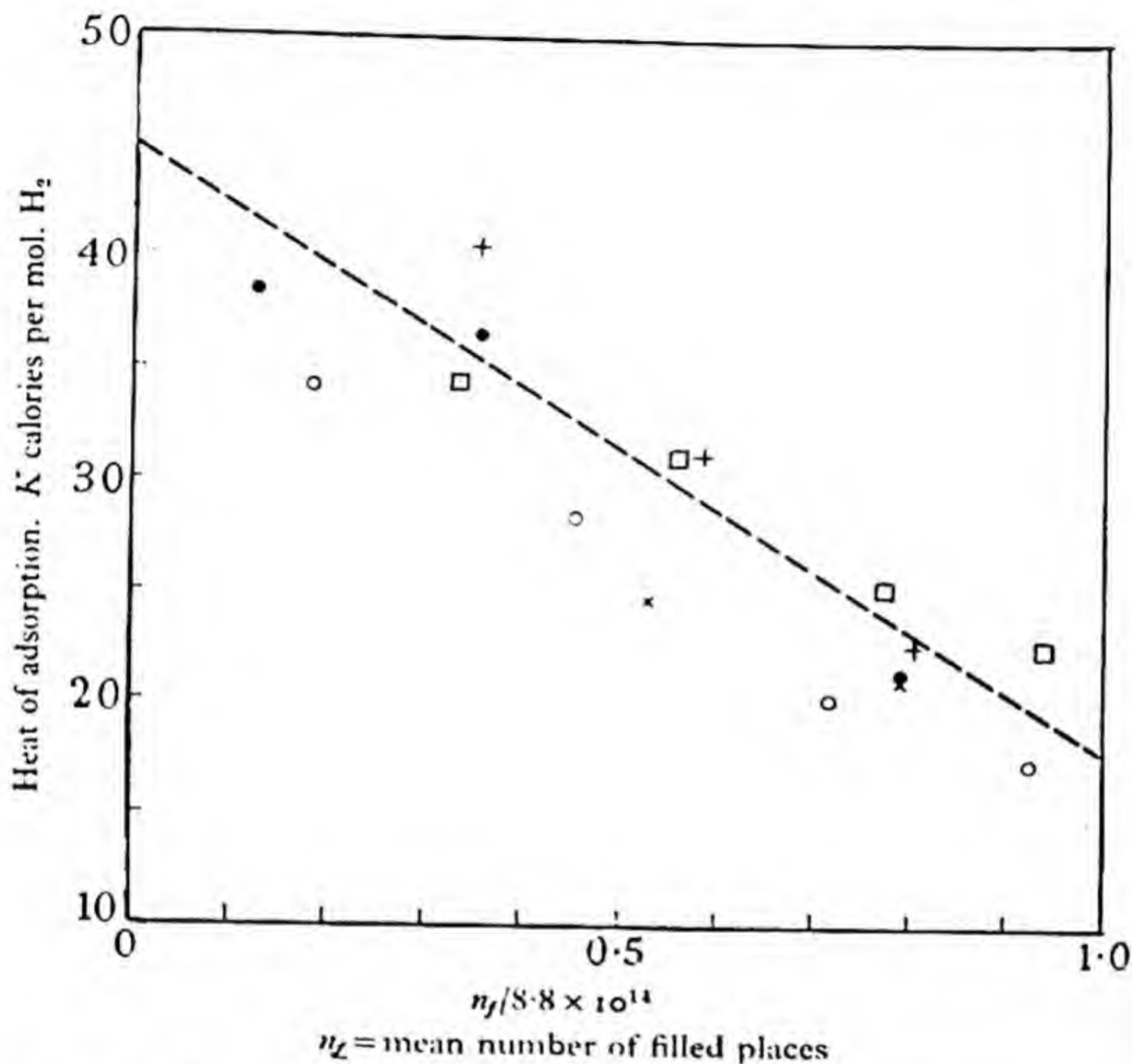


FIG. 4. Heat of adsorption per mole hydrogen as a function of surface covered.

From the dimensions and heat capacity of the wire the heat of adsorption could be calculated. Fig. 4 shows how this decreases from 45 kcal./mole hydrogen for a bare surface to 18 kcal./mole hydrogen for a nearly saturated surface.

With oxygen gas (4) a primary layer had a mean heat of adsorption of 139 kcal. and contained 4×10^{14} molecules. A secondary film was also detected with a heat of 48 kcal./mole oxygen which contained 0.9×10^{14} molecules. The method has also been used to detect adsorbed nitrogen (12).

4. Electrical Methods

J. H. de Boer (13) has summarized the early work of Langmuir on the effects of adsorbed films on thermionic emission from metal surfaces. This technique cannot give information about adsorbed films in the temperature range of interest in catalysis, say below 500°C . In this range one may detect adsorbed gases by a study of the photoelectric work function, or the contact potential. The first method offers difficulties, since with hydrogen and other gases the threshold is in the far ultraviolet. Some results for adsorbed hydrogen have been reported by Suhrmann and Csech (14) and Leypunsky (15). The second method is relatively simple to operate and has given a great deal of information in the hands of Bosworth and Rideal (6, 7). It was originally developed by Langmuir and Kingdon (16), who laid down conditions for its successful use. The reaction tube contains two tungsten wires, the emitter and collector, spotwelded to leads so that they cross at right angles with a separating gap of about 1 mm. An example of such a tube, in which the collector is a wire long enough to function as a catalyst filament, is shown in Fig. 5. For adsorption work only, a shorter collector as used by Bosworth is more suitable, since it heats up less under the influence of radiation from the emitter.

The tube is connected via a liquid air trap to a vacuum apparatus. The best results are obtained when a film of sodium is distilled over the inside of the tube, to act as a trap for oxygen. The whole reaction tube is normally immersed in liquid air. The filaments may be heated electrically by separate circuits, and an additional circuit allows a potential to be applied between the two wires and the associated thermionic current to be measured.

In his work on hydrogen films (7) Bosworth first cleaned both filaments by flashing *in vacuo*. The collector was allowed to cool, the emitter adjusted to a standard temperature, e.g., 2000°K ., and the thermionic current-polarizing voltage curve taken. This is curve A in Fig. 6. The emitter was now switched off, a dose of hydrogen admitted, a few seconds allowed for adsorption, and the apparatus evacuated. The emitter was switched on and the current-voltage curve again taken, curve B being obtained. The straight part of B is parallel to the straight part of A, but shifted to more

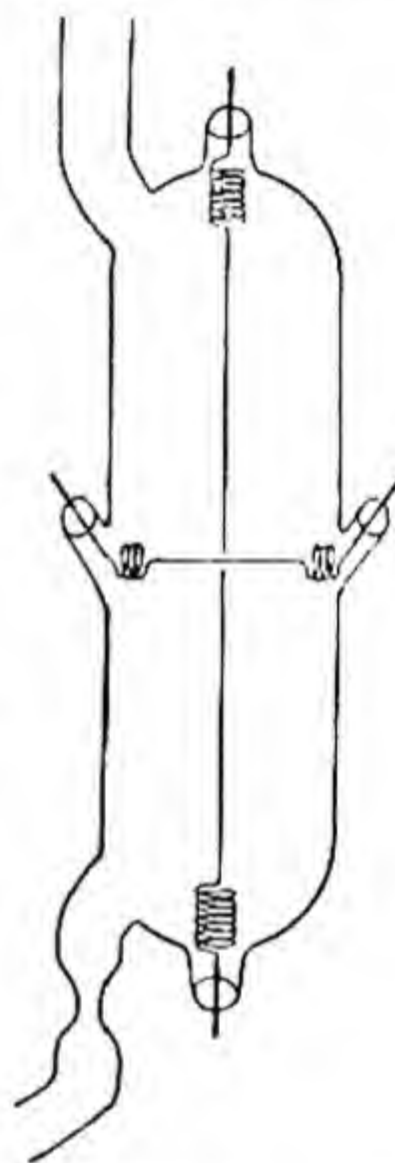


FIG. 5.
The measurement of contact potential. Reproduced from Eley and Rideal, *Proc. Roy. Soc. London* **A178**, 429 (1941).

positive potentials by an amount ΔV , which is minus the W-WH contact potential.

Bosworth obtained values for W-WH of $-1.04V$, W-WD, $-1.02V$ (7), W-WO, $-1.76V$, W-WN, $-1.38V$ (17).

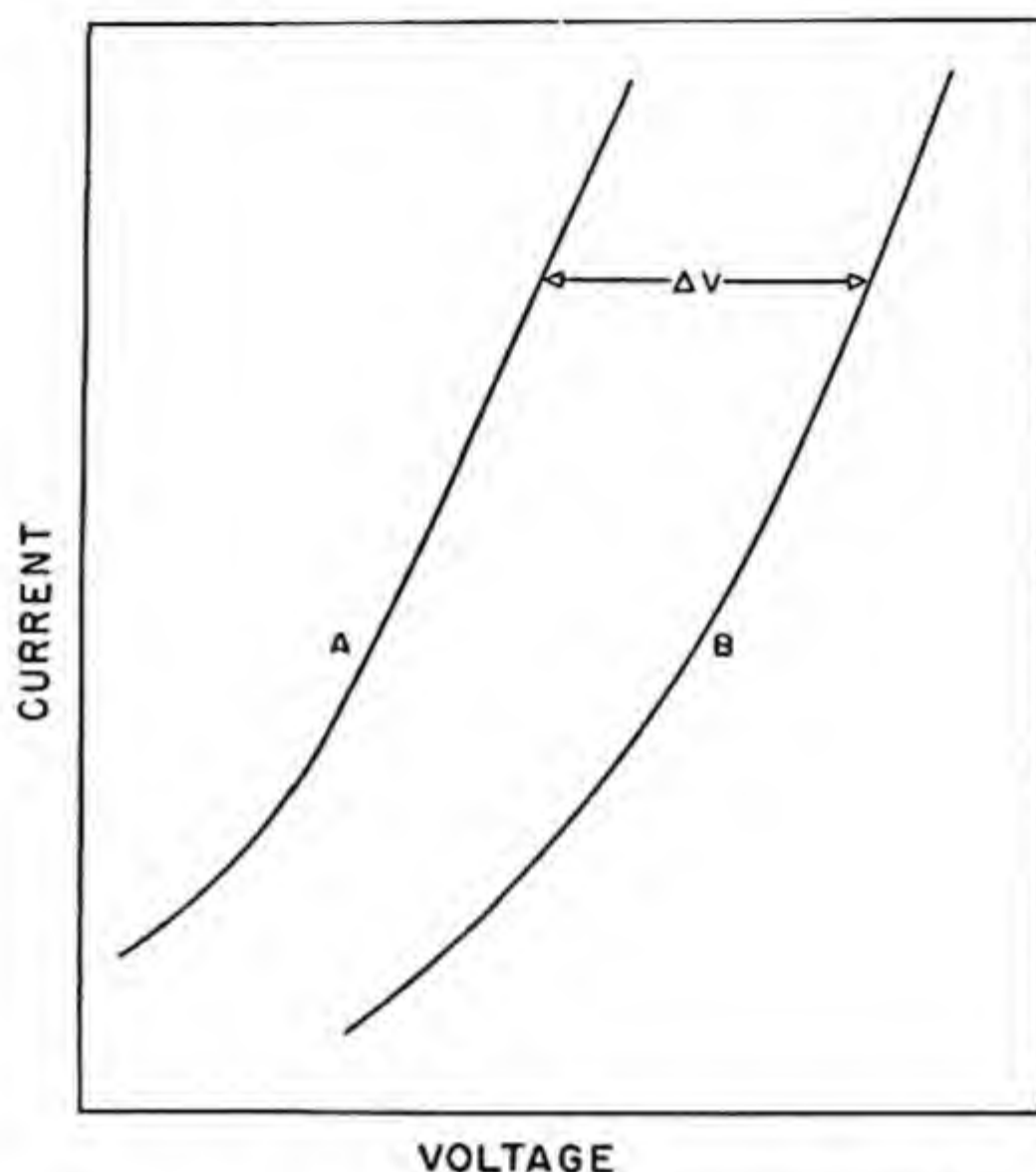


FIG. 6. Current-voltage curves for W-W(A) and W-WH(B) surfaces.

We may probably neglect the mutual depolarization of the adsorbed dipoles for hydrogen, nitrogen, and oxygen, when the dipole moment may be calculated by

$$\Delta V = 2\pi\mu c_s,$$

c_s being the surface concentration of dipoles, which for a saturated surface is usually taken as equal to the number of adsorption sites per square centimeter. It may, however, only be a definite fraction of this number. For hydrogen $\mu = -0.4D$ and for oxygen $\mu = -0.66D$, the sign indicating that the outer layer, hydrogen or oxygen, is negative. The method was used (17) to follow rates of evaporation of adsorbed monolayers of these gases.

5. Other Methods

It was reported in 1929 (18, 19) that hydrogen adsorbed on metals gave a characteristic electron diffraction pattern, but the work has not been followed up. In the ordinary electron diffraction apparatus one might

expect difficulties to arise from adsorption of impurities and desorption of hydrogen caused by impact of the high energy electrons. The most important use of this instrument to date would seem to be the determination of lattice orientation and spacing of the catalyst.

By bombardment with electrons adsorbed films of hydrogen have been found to possess an ionization potential of 13.4V (20, 21), but the effect is a complex one, and this value does not necessarily establish the presence of atomic hydrogen on the catalyst (22).

Eley (8) has shown how substantially clean tungsten surfaces of large area may be prepared by evaporation from a wire on to the walls of the reaction vessel. With a good high vacuum technique such films may be preserved free from adsorbed oxygen, and therefore unpoisoned, for a week or longer. Admission of hydrogen to such a film resulted in an immediate uptake of a quantity of gas measurable on a McLeod gage. The adsorption was irreversible and the gas could not be removed by pumping the film at 293° K. Since the true area of the film was unknown, it had to be determined by calculation from the observed uptake of hydrogen, assuming 1 hydrogen atom per tungsten atom in the surface. In other words, Roberts' results must necessarily be assumed to obtain the film area. The method, however, has confirmed Roberts' results on the speed of formation and stable nature of the chemisorbed film. Beeck *et al.* (9, 33d) have given similar confirmation for films of nickel and other metals. They have made the important observation that evaporation of the metal in the presence of inert gas leads to oriented films. It seems clear that the films are microcrystalline, the crystalline size depending on the conditions of evaporation (23a).

Frankenburger (23b) and coworkers have evaporated metal wires *in the presence* of gases. This calls to mind the classical study of Langmuir (23c) of the reaction between tungsten and nitrogen, which he showed to occur in the gas phase. Frankenburg found the reaction between iron and hydrogen to occur on the walls of the vessel. The conditions are complex but the method clearly merits further study.

Films thus offer a means of preparing clean surfaces of relatively low melting metals. Once a strongly chemisorbed film has been formed, however, it cannot be removed. Where this is desirable one can sometimes use the metal as a coat on a tungsten wire. In this way Bosworth (24) determined the Ni-NiO contact potential as $-1.4V$.

The classical method of study of hydrogen adsorption is, of course, to follow the uptake of gas by the powdered adsorbent by means of a manometer. Difficulties associated with this method concern the "cleaning" of the metal surface before adsorption, and additional gas uptake due to solution in the metal. These difficulties, realized in 1932, are still not

resolved, and the reader is referred to the Faraday Society Discussion of 1932 for a full account of the method and its results. Frankenburg (23d) has recently published a careful study of the system hydrogen gas-tungsten powder.

III. THEORETICAL STUDIES OF CHEMISORBED HYDROGEN ON METALS

1. *Time of Adsorption*

The known cases of chemisorption of gases on clean metal surfaces occur so rapidly that they must possess a negligible activation energy. They are quite different from the slow adsorptions, called "activated adsorptions," described by H. S. Taylor (25). Restricting our attention to tungsten, it has been found that tungsten powder, outgassed at 750° C., shows an "activated adsorption" of hydrogen (26) and nitrogen (27). The affinity of oxygen for a tungsten surface is such that we cannot expect to remove it by pumping the powder for a few hours at even 900° C.* In this connection Roberts (4) discovered that a tungsten wire covered with chemisorbed oxygen will show a slow uptake of hydrogen, which he attributed to a diffusion of oxygen into the interior, thus setting free sites for adsorption. This gives a plausible account of activated adsorption in this case. In this particular case there would also seem a possibility that the oxygen is reduced to water (28). Beeck *et al.* (9) have noted that a nickel surface will lose oxygen to the interior on standing, even in the absence of hydrogen. For metals, at least, we conclude that "activated adsorption" may be connected with the establishment of chemisorbed layers in the case of impure catalysts, but not with chemisorption on a clean metal surface, as put forward by Taylor (25). It follows, therefore that "activated" adsorption of hydrogen may be of significance for the initial process of activation of technical catalysts, but of less significance for catalytic reactions occurring in the established chemisorbed films. Further experiments on other systems, such as tungsten-methane, are required before we can generalize this picture. Furthermore, the author would restrict his opinion to metals, as the more complex metal oxide systems require separate consideration.

2. *Nature of the Chemisorbed Film (4, 5)*

In section II, 3 it was stated that a tungsten wire of apparent area 0.55 cm.² adsorbed at saturation 4.4×10^{14} molecules. Assuming a tungsten wire exposes 100 and 110 planes equally (29, 30), the surface would contain 6.65×10^{14} ρ tungsten atoms, the roughness factor ρ reasonably lying between 1 and 2. The film may therefore be either (a) made up of hydrogen

* Where a *bulb* is heated, one must also bear in mind diffusion of gases from the atmosphere through the walls.

atoms, 1 atom being held by each surface tungsten atom or site, or (b) made up of hydrogen molecules, 1 hydrogen molecule being held per site, and excluding the occupation of its four nearest neighbor sites. With Pauling's (31) values for the radii concerned, this would be so for the 110 plane, but on the 100 plane the molecules would probably pack with 1 molecule per site.

While structure (b) is not excluded by the evidence, structure (a) is more likely, since the high heat of adsorption would suggest the formation of chemical bonds. On present valency theory, it is difficult to see how molecular hydrogen could form a bond of the strength observed. For oxygen there are at least three possibilities for the primary film, and while Roberts originally considered (4) it to be atomic, he later considered (32) it to be molecular, of type (b). In this case the π electrons are available for bonding without disruption of the molecule into atoms. No evidence as to the nature of adsorbed films of other important gases, such as CO, N₂, CH₄, and C₂H₄ is yet available, apart from the relative adsorption values of Beeck *et al.* (9) on nickel films. These authors give as the number of molecules adsorbed per site CO, 1; H₂, $\frac{1}{2}$; N₂, $\frac{1}{2}$; C₂H₄, $\frac{1}{4}$; O₂, 2. The oxygen result they think is due to diffusion of oxygen under the surface. Ethylene, they suggest, is adsorbed with 1 hydrogen atom per site, but this method would scarcely give a strong bonding. If we allow for an ethylene molecule excluding the occupation of neighboring sites, as in Roberts' case (b) above, we find the observed result may arise in a number of ways, e.g.,

(1) Two point adsorption at the double bond. Twigg and Rideal's (33a) considerations suggest that on the 100 plane neighbor interactions might just be large enough to result in 1 in 4 occupation.

(2) One point adsorption of ethylene, either flat on the surface, or vertically as CH₃CH= or CH₂=CH— fragments.

It seems likely that other physical data, such as contact potentials, will be required to decide the mode of adsorption in cases like ethylene. As we shall see, data on the catalyzed exchange reactions of ethylene are most easily interpreted on the basis of two-point adsorption at the double bond. This is indeed what we should expect from the reactive character of the mobile π electrons.

W. G. Frankenburg (23d) has examined the adsorption of hydrogen on tungsten powder. From the strong decrease of heat of adsorption with surface covering, he has concluded that the first hydrogen is adsorbed as atoms, but subsequently the gas is taken up as molecules in "varying degrees of strain." He attempts to reconcile his results with Roberts' heats of adsorption on a wire, by assuming that Roberts' saturation value corresponds to 10–20% surface covering of the wire. This would require a roughness factor for the wire of 4.5, which is very unlikely, the value for a

tungsten wire similarly treated being only 1.35 (33b). The roughness factor may be supposed to lie somewhere between 1 and 2 (5). In a future comparison of this kind, further work on the roughness factor is necessary, and at the same time, consideration must be given to possible solubility effects in the uptake of gas by the powder, which would also lead to the kind of discrepancy found by Frankenburg.

In a recent paper, G. Halsey and H. S. Taylor (33c) discuss Frankenburg's results in the light of R. H. Fowler's treatment of adsorption. The data require, in their view, the hypothesis of a nonuniform surface. This may well be so for such a powder, but they are wrong to conclude that "heterogeneity is especially significant in the case of tungsten metal which has hitherto been treated as an essentially uniform surface." A completely aged tungsten wire may still be expected to be essentially uniform, whatever may be the case for the surface of the metal powder.

A paper by O. Beeck (33d) has only recently come to the author's notice. Working with evaporated films of metal of area of the order of 10,000 cm.² Beeck has confirmed all Roberts' results on the speed, extent, and heat of adsorption as a function of surface covered, for the adsorption of hydrogen on tungsten. Nickel shows a similar behavior. This makes extremely likely the view that adsorption on tungsten powder is complicated in some fashion, if not by solution, as suggested above, then by some kind of physical or chemical heterogeneity of the surface, as in the Halsey and Taylor picture.

3. *Mobility of the Chemisorbed Film*

Lennard-Jones (34) showed theoretically that lateral diffusion of adsorbed atoms would require an activation energy. The available evidence suggests a value for this one-quarter to one-third the evaporation energy of the hydrogen as *atoms*, i.e., about 20 kcal./g. atom. With this value we should not expect much lateral diffusion of atoms at temperatures equal or less than room temperature. Roberts' views on this important problem rest on his analysis of his heat of adsorption data (Fig. 4). He considers a quadratic lattice, and assumes the only interaction energy is a fixed energy V between nearest neighbors. This corresponds to a repulsive force, partly at least dipolar in nature. He distinguishes two extreme cases (5):

(a) The hydrogen molecules dissociate into atoms, which are immobile and remain on their original sites.

(b) The film is formed as before, but the atoms are supposed mobile and therefore move into positions of lowest energy.

If θ be the fraction of occupied sites, assumption (a) leads to the linear relationship found in Fig. 4.

$$q = q_0 - Z\theta V,$$

where q_0 is the heat of adsorption on the bare surface and Z , the number of nearest neighbors, is 4.

On assumption (b), however, up to $\theta=0.5$, the atoms may arrange themselves so that no two atoms are nearest neighbors. This may be seen by reference to Fig. 7.

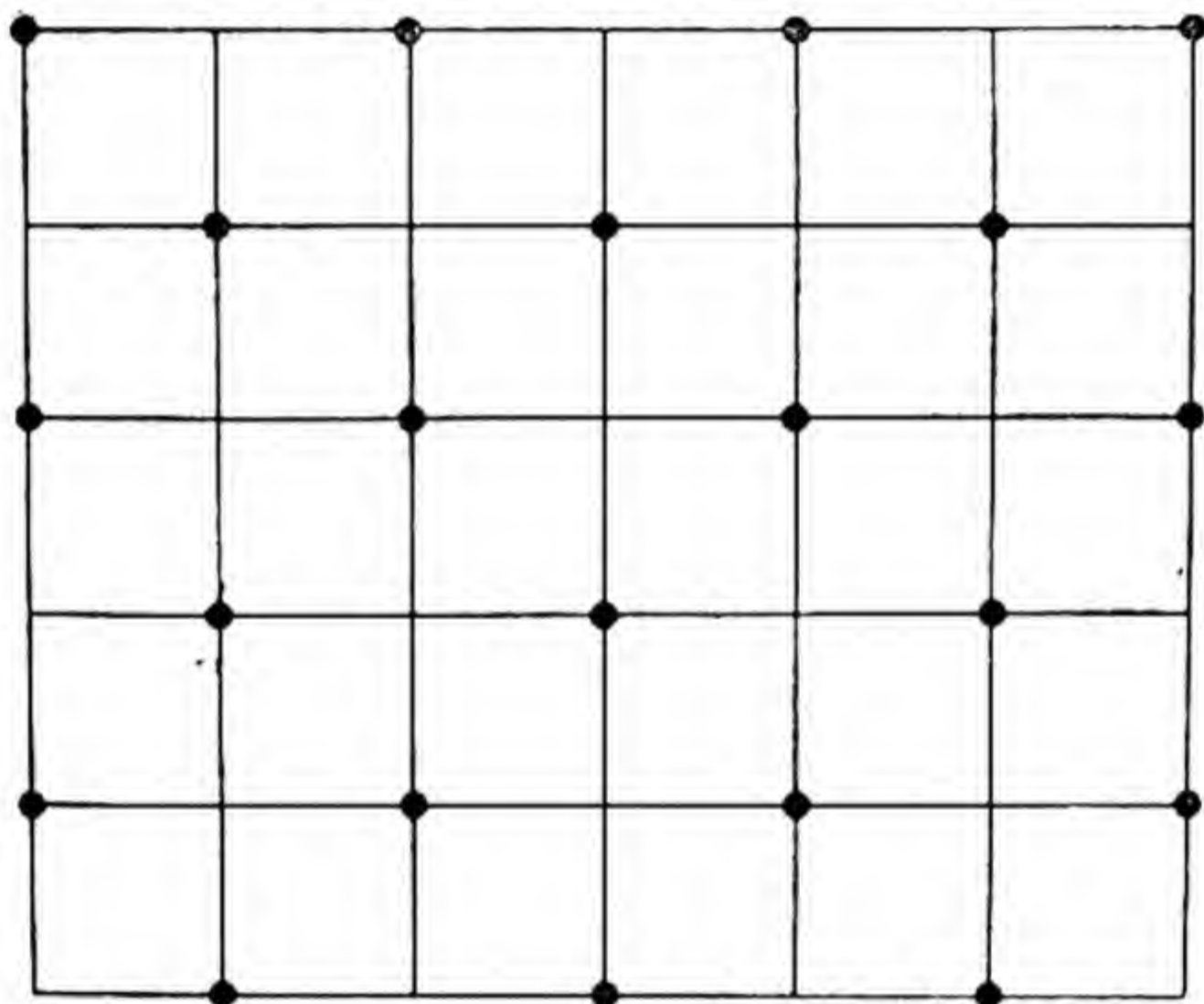


FIG. 7. Mobile atoms on a quadratic lattice.

Thus, $q=q_0$ up to $\theta=0.5$, at which point it abruptly falls to q_0-4V , as shown in curve a, Fig. 8. By taking account of Boltzmann's distribution, the corners of the curve are rounded to an extent depending on temperature, or more precisely, on $\eta = e^{-V/kT}$. Wang (35) has given a full treatment, obtaining the equation

$$\frac{q-q_0}{V} = -\frac{Z}{2} \left[1 - \frac{1-2\theta}{\{1-4(1-\eta)\theta(1-\theta)\}^{1/2}} \right]$$

Curves for various values of η are given in Fig. 8.

These considerations, based upon a fixed interaction energy V , thus definitely favor an *immobile* hydrogen film at room temperature. However, Miller and Roberts (36) refined the theory so as to allow for an alteration in V as the distance between adsorbed atoms changes because of thermal vibrations. Cases (a) and (b) now both give a very flat sigmoid, almost

linear, curve, and so the mobility of the hydrogen film at least at 293°K., remains an open question.

We may, however, suppose that at very low temperatures, e.g., 79° K., the hydrogen film is immobile. Roberts (4) has shown that the dissociative

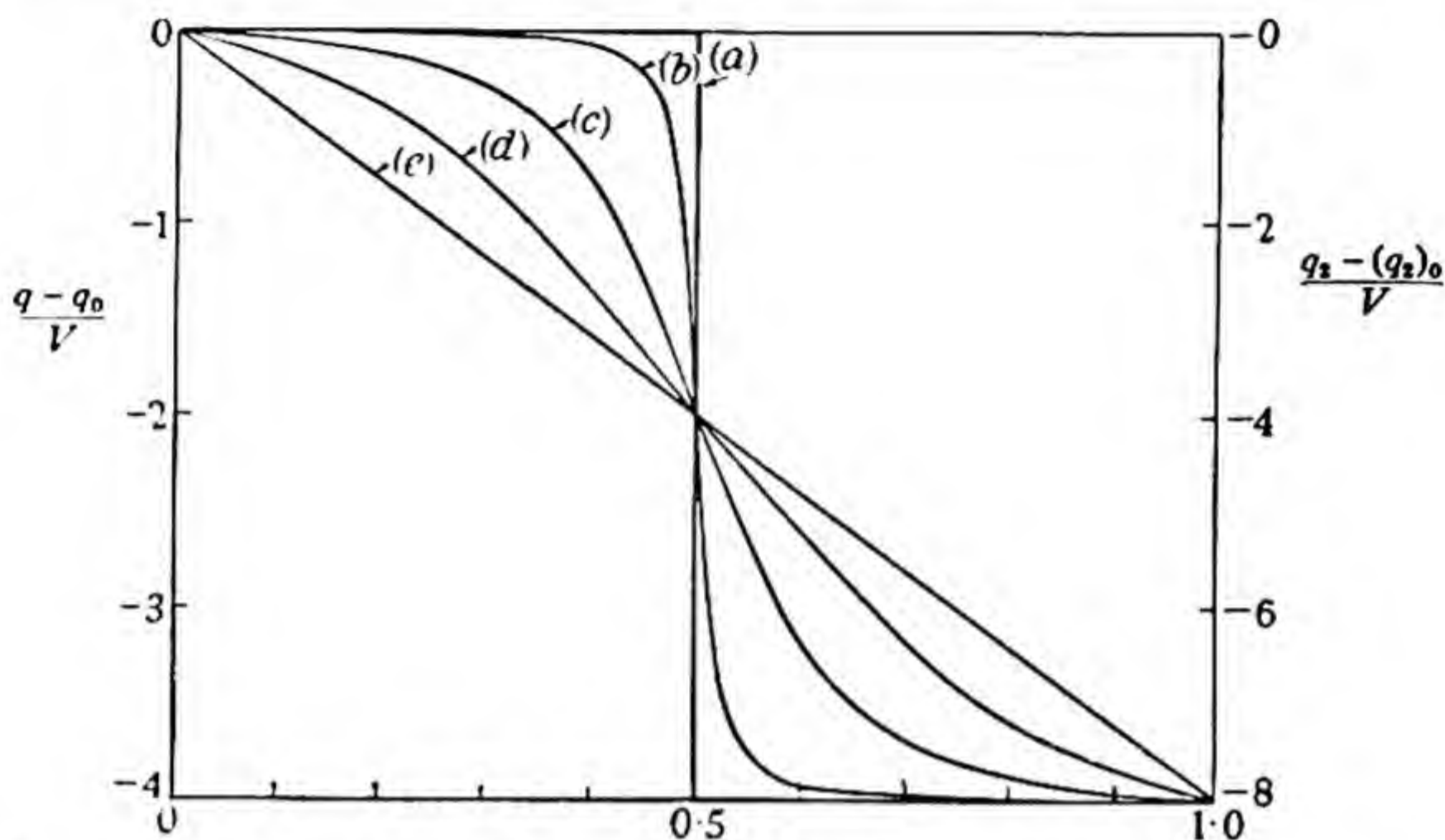


FIG. 8. Variation of heat of adsorption with fraction of surface covered. Curve (a), $\eta = e^{-V/kT} = 0$; (b), $\eta = 3.6 \times 10^{-3}$; (c), $\eta = 8.2 \times 10^{-2}$; (d), $\eta = 0.368$; (e), $\eta = 1$.

The scale on the left is for the heat of adsorption q when there is no dissociation and the one on the right is for the heat per molecule q_2 when there is dissociation. The subscript 0 refers to $\theta = 0$, and V is the interaction energy between particles adsorbed on neighboring sites. The calculations are for $Z = 4$.

adsorption of diatomic molecules to form an immobile atomic film results, on purely statistical grounds, in the complete film containing 8% empty sites or gaps. He also showed how gaps may arise in either mobile or immobile films, where the adsorbed molecule is so large that it excludes occupation of neighboring sites (3). He suggested that such empty sites might play a part in catalytic action, and catalytic mechanisms based on the assumed presence of gaps have been developed by Rideal (1).

4. Bond Type in the Adsorbed Film

Taking 103 kcal. as the dissociation energy of the hydrogen molecule, Roberts' adsorption heat of 45 kcal. gives a W—H bond strength (dilute film) of $(103 + 45)/2 = 74$ kcal./g. atom. Bosworth gives the dipole moment as 0.4 Debyes, the hydrogen being negative.

Calculations of the dissociative adsorption of hydrogen have been made

on carbon (37) and nickel (38), using the Polanyi-Eyring method (39). These calculations treat the surface atoms of the adsorbent as *free* atoms, and ignore the essential character of the metal electrons, which are not localized on definite atoms but exist in energy bands common to the whole crystal. The calculations do, however, indicate one way in which lattice spacing may affect the energy curve for adsorption.

We may suppose that it is essential to use a proper model for the metal. The adsorption of cesium on tungsten, a particularly simple case since the cesium ionizes completely on the metal surface, has been treated in this way most successfully by Langmuir (40) and de Boer (41). Catalysis requires a similar treatment for electronegative gases on metals, where the bond formed is largely homopolar, and not ionic as in the case of cesium.

The problem has been treated in an illuminating fashion by Lennard-Jones (34). He shows how an adsorbed atom at a metal surface will perturb the periodic potential field (due to the regular lattice of metal ions) in the neighborhood of the metal surface. This will lead to a local energy level in the metal surface next to the adsorbed atom and an electron in this level in favorable conditions will "exchange" with that in the adsorbed atom, leading to an essentially homopolar bond. Attempts have also been made to treat the surface energy levels of metals in the absence of adsorbed gases, by Tamm (42) and later workers. References to this work will be found in a paper by Shockley (43). Pollard (44) has endeavored to combine Tamm's considerations with those of Lennard-Jones. He has calculated the adsorption potential energy curve for hydrogen on a metal, finding an activation energy for adsorption similar to those discussed by Taylor (25). He considers that a one-electron bond will be formed (as in H_2^+), for the case where the energy levels are equal in the adsorbed atom and the surface metallic state. The general approach adopted is of great value.

The present author considers it essential that in theoretical considerations of catalysis the adsorption forces should be considered as arising from the metallic electrons, as indeed Polanyi (45) pointed out many years ago. For ethylene, for example, he would regard the π electrons in the adsorbed molecule as forming part of the electron gas of the metal. Such a concept does not involve the positive end of the dipole on the adsorbed atom. There is no conflict between the negative charge on adsorbed hydrogen on tungsten, and the existence of dissolved hydrogen as protons within a metal lattice (46). In each case the electrons lie in a metallic level, though in the adsorption case this level may be common only to the *surface* layer and not the whole metal. As Franck (47) observed, a dissolved proton must be surrounded by an electron swarm, otherwise the high ionization potential of hydrogen atoms precludes an explanation of the heat of solution observed. This notion applies equally to adsorbed hydrogen.

IV. PRODUCTION OF HYDROGEN ATOMS BY HOT TUNGSTEN

I. Langmuir (48) showed that if hydrogen gas were introduced into a bulb containing a heated tungsten filament, and the walls cooled in liquid air, a continuous decrease in pressure was observed. He supposed hydrogen molecules dissociated on the filament to give chemisorbed atoms, which evaporated and were trapped on the cold walls.



G. Bryce (49) reexamined the reaction, using a layer of molybdenum oxide on the walls of the vessel to trap the atoms. This method of trapping he found more efficient than the previous one. Over the temperature range 1148 to 1420° K. and pressure p 2.4×10^{-3} to 37×10^{-3} mm. mercury, n , the number of hydrogen atoms produced per cm.² per sec. is

$$n = 2.5 \times 10^{24} \cdot p^{\frac{1}{2}} \cdot e^{-\frac{45,000}{RT}}$$

Roberts and Bryce (50) consider two processes:

(a) The evaporation of atoms from the surface and the reverse process of adsorption of atoms from the gas.

(b) A hydrogen molecule strikes an empty site on the metal surface, one atom being adsorbed and the other returning to the gas phase. The reverse process is a gas atom striking an adsorbed atom and forming a molecule, which evaporates.

For *equilibrium*, θ the fraction of surface covered by atoms, for a hydrogen molecular pressure p_2 , is given by

$$\frac{\theta}{1-\theta} = A p_2^{\frac{1}{2}},$$

where A is a constant given by statistical mechanics. Equivalent values of A may be obtained by applying the principle of detailed balancing to processes (a) and (b).

$$A = \frac{10^3 K^{\frac{1}{2}}}{(2\pi m k T)^{\frac{1}{2}}} \cdot \frac{\alpha}{\nu} \quad \text{Process (a)}$$

$$A = \frac{(m_1/m_2)^{\frac{1}{2}}}{10^3 K^{\frac{1}{2}}} \cdot \frac{\delta}{\gamma} \quad \text{Process (b)}$$

K is the equilibrium constant in atmospheres for $\text{H}_2 \rightleftharpoons 2\text{H}$ in the gas phase. m_1 is the mass of a hydrogen atom, m_2 that of a molecule, α is the probability that an atom striking a bare site is adsorbed, ν the probability that an atom will evaporate, δ the probability that a molecule striking a surface will split up into an adsorbed and a gaseous atom, and γ the probability of the reverse step to the last named.

Process (a) then yields for the rate of production of atoms, ν ,

$$\begin{aligned} \nu &= \nu \theta \\ &= \nu A p_2^{\frac{1}{2}} = \frac{10^3 K^{\frac{1}{2}} \alpha p_2^{\frac{1}{2}}}{(2\pi m_1 k T)^{\frac{1}{2}}} \quad \theta \ll 1 \end{aligned}$$

Process (b) yields

$$v = \frac{p_2 \delta}{(2\pi m_2 k T')^{\frac{1}{2}}} (1 - \theta)$$

$$= \frac{p_2^{\frac{1}{2}}}{A (2\pi m_2 k T')^{\frac{1}{2}}} = \frac{10^3 K^{\frac{1}{2}} \gamma p_2^{\frac{1}{2}}}{(2\pi m_2 k T')^{\frac{1}{2}}} \quad \theta \sim 1$$

Thus a kinetic equation of the correct order may arise either from process (a) with a low surface covering θ , or from process (b) on a nearly saturated surface ($\theta \sim 1$). In each case the main effect of temperature is exerted through the term $K^{\frac{1}{2}}$. Assuming the observed velocity at 1420°K. , the authors calculated the velocity at the other temperatures using Giaque's data (51) and a value for the dissociation energy of hydrogen of 101 kcal. The results are shown in Table I, indicating a good agreement with experiment.

TABLE I

Velocity of Production of H atoms, v , in atoms per square centimeter per second at $p_2 = 12.5 \times 10^{-3}$ mm. mercury

T°K.	$v \times 10^{-14}$	
	Obs.	Calc.
1420	316	(316)
1338	115	103
1243	32	22
1148	7	4

Bosworth (7) determined the contact potential of a tungsten filament under the above conditions, deducing that θ lay in the range 0.6–0.9. It was therefore concluded that for the conditions concerned, mechanism (b) was operative.

The experimental conditions departed from the equilibrium conditions assumed in the above theory, but we may suppose the resulting error is small. Other workers (52) have attempted to reconcile process (a) with Bosworth's result by assuming the reaction occurs on "active centres." As we shall see, a variation in activity over a tungsten surface is detectable in surface exchange reactions at 77°K. , but the variation is so slight that it is undetectable at 193°K. At 1100°K. there is therefore every reason to believe the tungsten surface is uniform in its activity.

V. RECOMBINATION OF HYDROGEN ATOMS

Bonhoeffer (53) used a thermometer bulb coated with a thin film of the catalyst. On exposure to a stream of hydrogen gas containing atoms, the thermometer reached a temperature which depended on the efficiency of

the catalyst. The metals in order of decreasing efficiency were palladium, platinum, silver, tungsten, iron, copper, calcium, lead, and mercury, which is the order of their hydrogen overvoltage. He concluded that the atoms recombined in the adsorbed layer to evaporate as molecules.

Roginsky and Schechter (54, 55) found that the recombination of atoms possesses a small, though definite, activation energy. This, together with the specificity exemplified in the series above, shows that the catalyst is not functioning as a mere third body for the removal of the energy of reaction. These authors are in favor, for their experimental conditions, of a mechanism involving a gas atom striking an adsorbed atom and evaporating as a molecule. This fits in with Bryce and Roberts' mechanism for the production of hydrogen atoms.

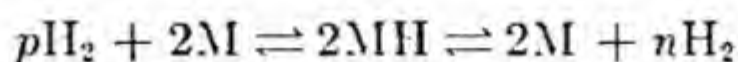
VI. THE PARAHYDROGEN CONVERSION

1. Early Work

In their classical paper Bonhoeffer and Harteck (56) distinguished between the catalysts charcoal and platinum black, both of which are active in causing the conversion reaction parahydrogen \rightleftharpoons orthohydrogen. Charcoal is most efficient at low temperatures, and is therefore used to prepare parahydrogen at 77° K. or lower temperatures. Platinum black is inefficient at low temperatures, but its efficiency increases with temperature. It was subsequently possible (57) to distinguish two mechanisms, which we may call the paramagnetic and chemical mechanisms. Active charcoal was considered to be a paramagnetic catalyst, that is, the hydrogen was converted by the magnetic field of the unsaturated surface atoms of the catalyst. This mechanism was established for two classes of homogeneous catalyst, paramagnetic gases and paramagnetic ions in solution (58), and treated theoretically by Wigner (59). According to Wigner, the transition probability is little affected by temperature, so that the conversion rate depends mainly on the concentration of hydrogen molecules in the van der Waals layer, which increases with decrease of temperature, to give the result observed. Paramagnetic metal oxides were also found to be effective in this way, but diamagnetic oxides less so (60). Particularly convincing is the result that oxygen adsorbed on charcoal at low temperatures, and therefore presumably in the form of paramagnetic molecules, promotes the conversion. If the oxygen is adsorbed at higher temperatures it exerts a poisoning effect, attributed to adsorption as atoms (57).

The chemical mechanism (61, 62) was supposed to involve the dissociative chemisorption of hydrogen molecules, in a *loosely bound fashion*. In this mechanism, the hydrogen, dissociated into atoms on the surface of the catalyst, recombined to give normal hydrogen, i.e., a mixture in which the

ortho/para ratio had the equilibrium value for the temperature of experiment.



A parallelism was drawn with Taylor's notions about activated adsorption. The reaction $\text{H}_2 + \text{D}_2 \rightarrow 2\text{HD}$ on nickel (63) was found to possess similar kinetics to the conversion, and the same mechanism was proposed for this reaction. On the other hand, this reaction did *not* go on charcoal at low temperatures (64, 65), thus confirming the paramagnetic mechanism in this case. The work up to 1935 is admirably summarized in the book by A. Farkas (66), and we restrict ourselves to a consideration of more recent work.

2. The Paramagnetic Mechanism

The original explanation still holds good. It has, however, occurred to the author that the normal method of comparing the conversion with the $\text{H}_2 + \text{D}_2$ reaction does not allow a completely unequivocal decision as to whether the conversion is paramagnetic or not, at temperatures as low as 77° K. Chromium oxide at this temperature shows a very rapid conversion, but a relatively slow $\text{H}_2 + \text{D}_2$ reaction (64). A difference of activation energy of 1.2 kcal. such as *may* arise from zero point energy effects (63) would cause the $\text{H}_2 + \text{D}_2$ reaction to go more than a thousand times more slowly than the conversion at this temperature, if the latter involved only the chemical mechanism.

While the paramagnetic substances hemin, hematin, and copper phthalocyanine catalyze the conversion at room temperature, the diamagnetic hematoporphyrin and metal-free phthalocyanine are inactive (67). No catalysis was found for the $\text{H}_2 + \text{D}_2$ reaction. Since the surface area of the hemin crystals could be estimated, the collision efficiency of the conversion could be calculated. The value of 10^{-10} so determined is in reasonable agreement with Wigner's theory (59).

Burstein (67) has found that very pure charcoals stringently outgassed at 900° C. become very active catalysts for the $\text{H}_2 + \text{D}_2$ reaction at liquid air temperature. Her conclusion was that the conversion involves an exchange mechanism similar to that reviewed in the next section. One is much inclined to suppose that the paramagnetic conversions observed on the earlier charcoals were due to adsorbed impurities rather than to surface free valencies. We might expect that the surface was saturated with chemisorbed oxygen, with some normal oxygen molecules held firmly over gaps in this layer and active as paramagnetic centers. A temperature of 900° C. is required to free a tungsten surface *slowly* from oxygen, and a similar result may hold for charcoal. Thus, Burstein's stringent outgassing may

have given a clean surface which could chemisorb hydrogen and convert parahydrogen by the mechanism below.

Turkevich and Selwood (68) have examined the conversion on the solid free radical α , α' -diphenyl- β -picryl hydrazyl. This substance did not show a very strong van der Waals' adsorption of hydrogen, and its efficiency as a catalyst was much increased by mixing it with zinc oxide, which by itself was a powerful adsorbent but a weak catalyst.

3. The Chemical Mechanism

a. *The Surface Interchange Reaction.* The original term "high temperature mechanism" is a misnomer now we know that the conversion can go through this mechanism at 77° K. on tungsten (8, 28), charcoal (67) and chromium oxide (64).

A. Farkas (69) found the parahydrogen conversion was catalyzed by a tungsten wire and described his results in terms of the dissociation and recombination of hydrogen in a loosely bound chemisorbed layer. Roberts' results on the stability of the chemisorbed film showed that this mechanism was unlikely to hold for the specific catalyst and conditions concerned (70). The rate of combination of chemisorbed atoms at room temperature is immeasurably slow and cannot account for the extremely rapid conversion observed. In reply, Farkas suggested (71) that most of the chemisorbed hydrogen was inactive, the conversion proceeding by his mechanism for a few active spots, not detectable in Roberts' work.

The matter was subjected to experimental test by Eley and Rideal (8, 28). While Farkas (69) had shown the need to flash a tungsten wire at 2500° K. to make it catalytically active, it seemed desirable, in view of the known activity of bulk oxides, to establish the absence or otherwise of surface oxide from the active wire by means of an independent physical method. A stringent high vacuum technique was used, and the contact potential method adapted to measuring the concentration of adsorbed oxygen on the catalyst wire. The reaction vessel, with its long catalyst (collector) filament, and its short emitter filament, has been shown in Fig. 5. With the long collector it was conveniently found that the heat radiation from the emitter generated a sufficient temperature to evaporate hydrogen from a mixed surface film of hydrogen and oxygen on the collector. The temperature reached was insufficient to evaporate the oxygen, the surface concentration, c_s , of which was calculated from the observed contact potential ΔV by $\Delta V = 2\pi\mu c_s$, where $\mu = 0.66D$. The procedure was to clean both filaments, form an oxygen film on them, and then to flash the oxygen off the emitter. The catalyst filament was then heated until its contact potential indicated the required c_s value. Both filaments were then brought to bath temperature (77° K.), parahydrogen admitted, the catalyst

wire switched on to give its standard operating temperature of 142°K. , and the parahydrogen conversion followed as a function of time. As in all other cases, a first order constant k described the course of the reaction. At the end of the experiment, the tube was evacuated and the contact potential, and thus c_s , checked. The contact potential for a full oxygen film, primary film plus oxygen on the gaps, was found to be $-1.74V$, and a value of $-1.22V$ was attributed to the primary film. A mere removal of oxygen from gaps did not allow the conversion to proceed, but the activity of the surface increased strongly as the primary chemisorbed oxygen was removed, as shown in Fig. 9.

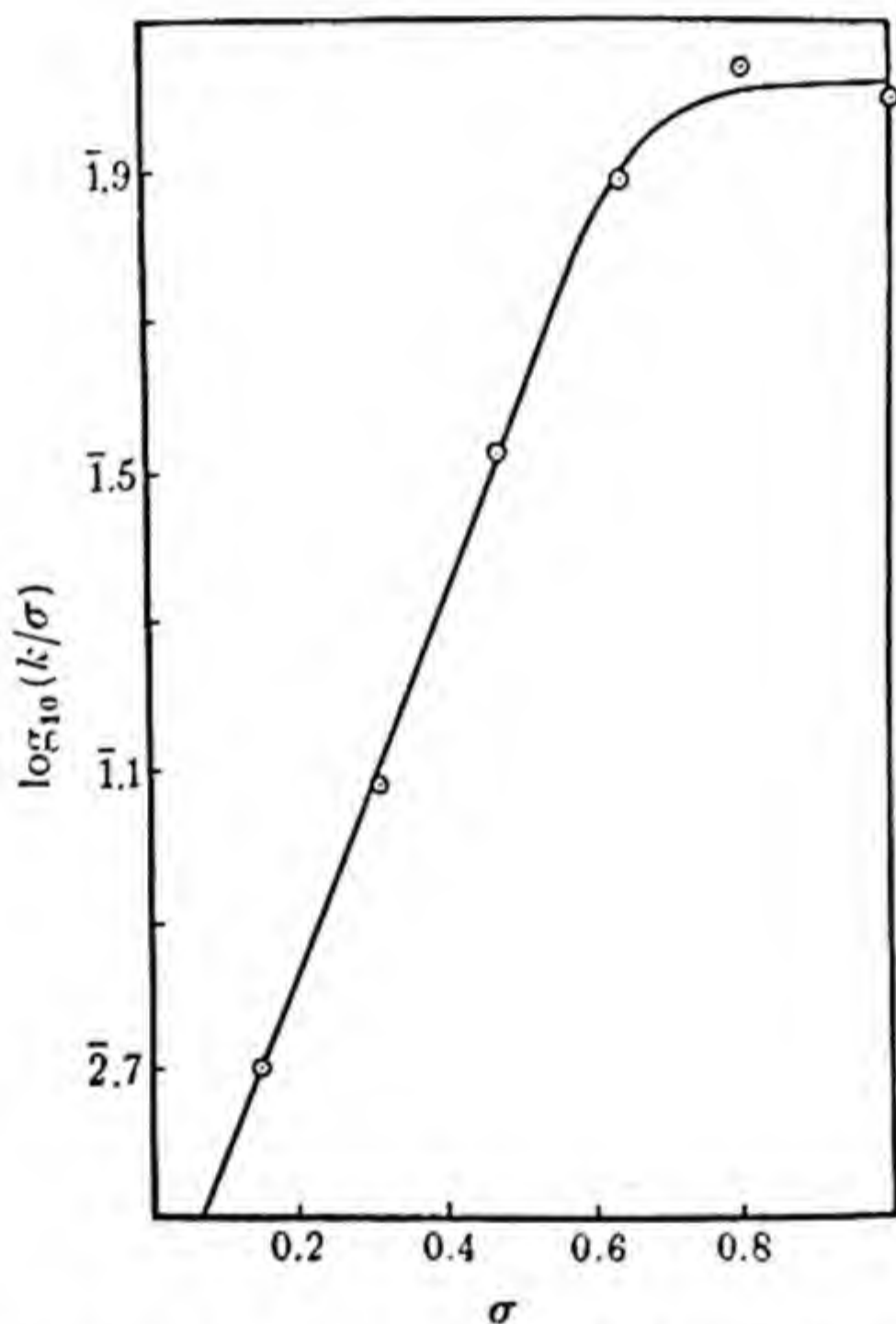
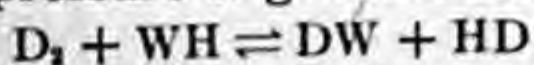


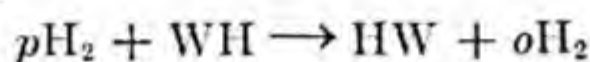
FIG. 9. The relationship between reaction constant per unit surface bare of oxygen, and the fraction of surface σ free from oxygen. Reproduced from Eley and Rideal, *Proc. Roy. Soc. London A178*, 429 (1941).

It is clear from Fig. 9 that the clean metal surface is an active catalyst for the conversion, and it therefore follows that the most likely mechanism is an exchange of atoms between molecularly adsorbed hydrogen and the underlying primary layer of chemisorbed atoms. This notion was shown to be correct by examining the interchange reaction between a hydrogen covered surface and a low pressure of gaseous deuterium (8).



A clean tungsten surface of sufficient area (400 cm.^2) was secured by evaporation from a wire. Hydrogen was admitted and immediately exhausted, leaving a chemisorbed hydrogen film on the tungsten. Deuterium gas was then admitted at 0.2-mm. pressure. Both at 293° K. and 193° K. a rapid exchange of atoms was found. At 77° K. the equilibrium favored adsorbed hydrogen, and it was necessary to contact hydrogen gas with the surface deuteride, when a rapid exchange was observed.

The atomic exchange reaction proceeded with a similar velocity to the parahydrogen conversion, thus establishing the identity of the latter as a surface exchange reaction.



Certain details are of great interest. All the chemisorbed hydrogen was shown to be active in the surface exchange (and therefore conversion) reaction at 293° K. From the initial amount of chemisorbed hydrogen one may calculate a film area of 428 cm.^2 By measuring the amount of hydrogen appearing in the gas phase with increasing deuterium pressure the results shown in Fig. 10 were obtained. At higher pressures a constant amount of

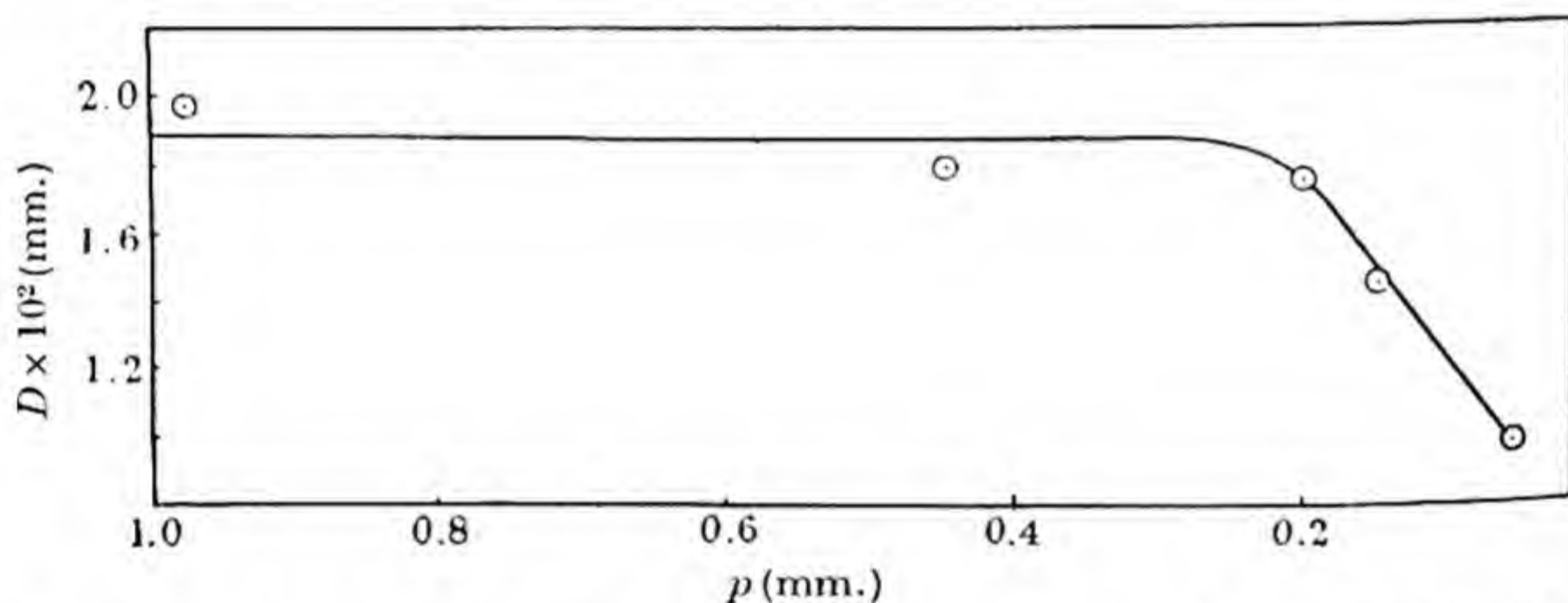


FIG. 10. To show how the amount of interchange between gaseous D_2 and a WH surface (D) is affected by the pressure of D_2 gas. Reproduced from Eley, *Proc. Roy. Soc. London A178*, 452 (1941).

exchange was obtained which corresponded to the equilibrium shown above being forced completely over to the right. This amount was 2.18×10^{17} molecules, and taking 1.2×10^{15} sites/ cm.^2 , this gave a film area of 364 cm.^2 Since reaction volumes were calculated and not calibrated, the agreement with the first figure is as good as may be expected.

At 77° K. only 20–30% of the chemisorbed deuterium exchanged in the time of experiment, i.e., 6 minutes. Thus, all the sites were not equally active at this temperature. Since the difference was undetectable at 193° K. , we may suppose the difference in activation energy between active

and inactive planes is not greater than 500 cal./mole. The different sites may be associated with the two common planes 110 and 100. Poisoning the film cut down the amount of exchangeable hydrogen and the conversion velocity in approximately the same ratio. Thus, we see that at temperatures $\geq 193^\circ \text{K}$. all the chemisorbed hydrogen may be taken as active in causing the conversion (or $\text{H}_2 + \text{D}_2$ reaction) by the exchange mechanism.

A. and L. Farkas (72) have examined the conversion and surface exchange reactions on evaporated films of nickel, platinum, and palladium. The two reactions have identical rates on nickel at 293°K ., while for platinum the exchange is the slower reaction by a factor 5 and for palladium by a factor 15. It is clear that the conversion on nickel goes through the exchange mechanism. In the present author's opinion this conclusion may also be valid for the other two metals, since it is extremely unlikely that two such different mechanisms would have a velocity within a factor as large, even, as 15. The discrepancy might be a zero point energy effect, and a detailed investigation of these metals is planned. Farkas and Farkas refer to a possible dissociation of hydrogen on top of the stable chemisorbed layer, but there are no good physical grounds at present for this postulate.

b. *Chemisorbed Films of "Foreign" Gases*. The parahydrogen conversion on a clean tungsten wire is quite rapid at 142°K ., but the admission of a trace of carbon monoxide, nitrogen, oxygen, or ethylene results in the formation of adsorbed films which effectively poison the reaction at this temperature. On raising the temperature of the poisoned wire, conversion sets in at the following approximate temperatures, carbon monoxide at 223°K ., nitrogen and oxygen at 273°K ., and ethylene at 473°K . For all gases except oxygen the effect was reversible, a return to the lower temperature showing the wire to be still poisoned. Oxygen, however, was removed in some way on heating in hydrogen at 273°K .

It is not clear how far conversion on these films proceeds at gaps in the film, or actually *on top* of the film. Since carbon monoxide may be expected to yield a chemisorbed film without gaps, the latter hypothesis may be true. If true this will be an important development of catalyst theory. Experiments are planned to decide the point.

c. *Absolute Rate of the Conversion*. In a paper submitted for publication, Eley (73) gives a calculation of the "temperature-independent" factor of the first order constant k . He assumes that:

(a) Conversion occurs through an exchange of atoms between a molecule in a van der Waals' layer and an adjacent atom in the underlying chemisorbed layer.

(b) The surface atoms are of uniform activity.

(c) The van der Waals' layer is a mobile monolayer of hydrogen molecules on localized sites, neighbor interactions being neglected.

(d) The ratio of partition functions of the chemisorbed atom and the transition complex (H_3) is unity.

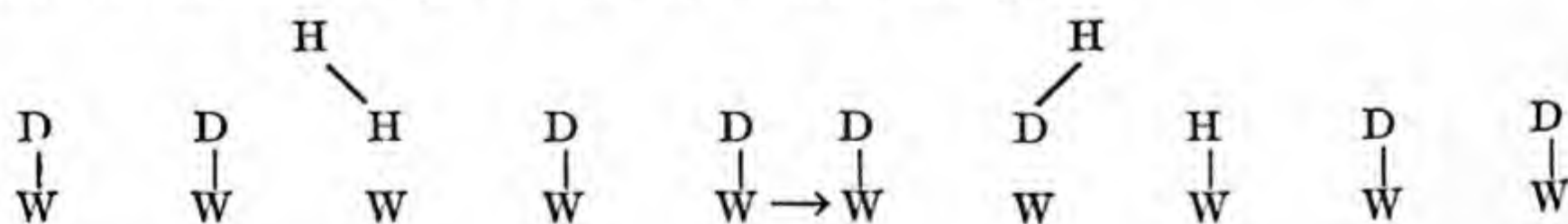
The method was to calculate the concentration of molecules in the van der Waals' layer by statistical mechanics, and to formulate the rate of exchange by activated complex theory (52). The results for the "temperature-independent" factor B , in $k = B \cdot e^{-E/RT}$, for a catalyst area of 1 cm.^2 , a reaction volume of 300 cc. , and a hydrogen pressure of 20 mm. mercury , are shown in Table II.

TABLE II
Rate of the Parahydrogen Conversion

Catalyst	$B \cdot \text{min.}^{-1}$ (calc.)	$B \cdot \text{min.}^{-1}$ (expt.)
W wire	170-40	27
Pt wire	90	110
Pd disc	100	53
Ni tube	100	31

Much lower values of B are found for pyrex glass, which are reasonably explained on the idea of a few sparsely scattered centers of activity. Much higher values of B may be shown to arise for a surface of sites of graded activation energy. Such high values of B are associated with anomalously high values of the activation energy, a case in point being the earliest result of Bonhoeffer and Farkas (74) for a platinum wire.

The detailed mechanism of the interaction between molecular and atomic hydrogen is still an open question. E. K. Rideal (1) has suggested an elegant mechanism, which makes use of an assumed 8% empty sites in the chemisorbed layer. A hydrogen molecule held over a gap is supposed to undergo a valency switch, the new $W-H$ formed helping to overcome reaction inertia and give a low activation energy.



This mechanism would lead to a mobility of gaps, which, as two gaps came together, would be filled up by adsorbing a molecule and thus the reaction would self-poison. On tungsten, however, we might expect the ratio, conversion rate to poisoning rate, to be of the order of 10,000 and only detectable in specially planned experiments (73). A poisoning action of hydrogen has been described for iron (75) and charcoal (76), but it is not clear how far the conversions observed involved the paramagnetic mechan-

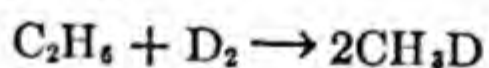
ism. The mechanism may be tested by filling the gaps with carbon monoxide or hydrogen atoms, which, on this view, should poison the conversion.

The general position regarding the reactivity of a chemisorbed hydrogen atom is quite striking. These atoms, in spite of their strong bond to the tungsten surface, are as reactive at 77° K. as free gaseous atoms at 900° K. The present author (73) holds the tentative view that the energy of the activated complex is depressed by the action of resonance, a consideration advanced in general terms by Polanyi (77).

VII. THE EXCHANGE OF ATOMS BETWEEN DEUTERIUM GAS AND HYDRIDES

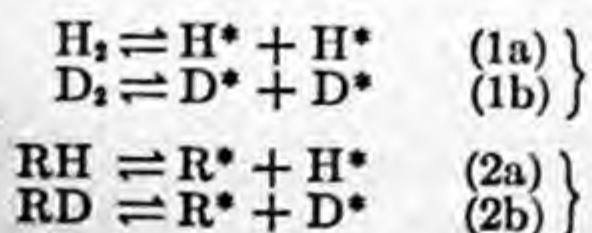
J. Horiuti and M. Polanyi (78) discovered that platinum black catalyzed the exchange of atoms between deuterium gas and liquid water. A. and L. Farkas and E. K. Rideal (79) discovered the exchange between deuterium and ethylene catalyzed by nickel, to be discussed in section VIII.

One of the clearest cases is the exchange reactions of methane and ethane on active nickel catalysts, investigated by Morikawa, Benedict, and Taylor (80). Methane exchanges with methane-d₄, deuterium, and deuterium oxide, the rates at 184° C. decreasing in the order given. It seems clear that the methane is chemisorbed by rupture of the C—H bond. The activation energy of 19 kcal. for the exchange with methane-d₄ is attributed to the energy of desorption of methane. The slower reaction with deuterium has an activation energy of 28 kcal., and the slower rate is attributed to the deuterium being strongly adsorbed and displacing methane from the surface. While ethane exchanges with deuterium at an appreciable rate at 110° C., bond scission producing heavy methane only becomes appreciable at 150° C.



There is thus a difference of 50° C. between the activation of the C—H and the C—C bond, and it is interesting that the weaker C—C bond requires the higher temperature.

Farkas and Farkas (81, 82) assumed that the rate of dissociation of hydrogen molecules on the catalyst was measured by the parahydrogen conversion. They further assumed that the hydride was adsorbed by dissociation of a hydrogen atom, and that hydrogen and hydride competed for the chemisorbed layer.



The asterisk is meant to indicate a chemisorbed atom or radical. Where

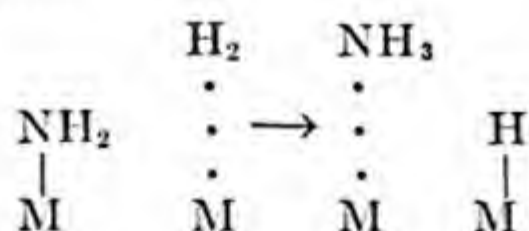
the observed conversion was faster than the exchange, the rate of dissociation of hydride (2a) was supposed to be the determining step. Where the two rates were the same, the dissociation of deuterium (1b) limited the rate of exchange. In the case where the hydride was water, adsorption isotherms were worked out (83). A very good example of their method is given in the case of ammonia (84).

The new knowledge about the parahydrogen conversion indicates the need for a reconsideration of these views. Much more work is required, but it may be supposed that in the presence of other gases the conversion is proportional to (a) the concentration of chemisorbed hydrogen atoms and (b) the concentration of hydrogen molecules adsorbed in the van der Waals' layer, or perhaps more specifically on gaps in the chemisorbed layer.

The "foreign" gas molecules will compete with hydrogen for sites in the van der Waals' layer. Competition for the sites in the chemisorbed layer is rather less likely, requiring, as it would, a rather close concordance of two large free energies of chemisorption. At present one might suppose that the chemisorbed layer will consist largely of either the hydride or hydrogen. Of course, if it is hydride the layer will contain 50% hydrogen atoms, assuming the R—H bond is broken in the process of chemisorption.

The parahydrogen conversion on this view is then, broadly, a test for the presence of chemisorbed hydrogen atoms. The effect of an increased pressure of hydride in decreasing the velocity of parahydrogen conversion is to be attributed in the first place to a displacement of hydrogen by hydride from the van der Waals' layer.

The author does not wish to press these views, but merely to indicate the lines along which his own work will be directed. If we consider the exchange with ammonia (84) it is his view that the chemisorbed layer is likely to be largely *either* ammonia (held perhaps as H and NH₂ fragments) or hydrogen atoms. It is not possible to predict which of these two it will be. If we hold the hydride at constant pressure, and increase the hydrogen pressure a hundredfold, we can only expect a noticeable displacement of chemisorbed hydride if the free energies of chemisorption of hydride and hydrogen lie within 5 kcal. or so. If this be so, then a displacement process can occur, perhaps of the kind



In the case of ammonia exchanging with deuterium on an iron catalyst the facts (84) are:

(a) The absolute rate of exchange is independent of the ammonia

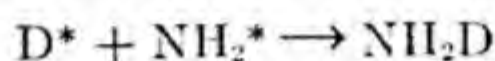
pressure and approximately proportional to the square root of the deuterium pressure.

(b) Small amounts of hydrogen (but not nitrogen) are formed when ammonia is contacted with an iron catalyst.

(c) The conversion of parahydrogen goes rapidly on the clean catalyst. It is reversibly inhibited at 100° C. by the presence of ammonia, but even then is much faster than the observed exchange reaction. At room temperature it is irreversibly inhibited by adsorption of ammonia.

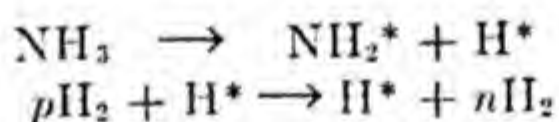
(d) The activation energy of the conversion is 8 kcal. and the exchange is 15 kcal.

Farkas supposes that mechanism (2b) above, namely,

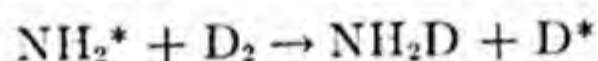


determines the rate of exchange, the ammonia being strongly and the hydrogen weakly chemisorbed.

This scheme is easily modified to take account of the new view of the conversion and the stability of chemisorbed layers. The ammonia is adsorbed as NH_2 and H fragments as before. Parahydrogen conversion can proceed, though at a reduced rate, on such a film by exchange with the chemisorbed hydrogen from the ammonia.



The exchange reaction may involve some process such as the following one, making use perhaps of empty sites



The effect of pressure on the exchange rate would then depend on the concentration of deuterium in the van der Waals' layer or over gaps in the chemisorbed layer.

Such a view can only be tentative in the absence of further experimental work. Roberts (4) has shown how oxygen will displace chemisorbed hydrogen from tungsten. Here we pass from a full hydrogen layer to a full oxygen layer, the latter being more firmly bound. We require more work along this line for other gases, before we can be sure of our catalytic mechanisms.

For the same reasons, the exact mechanism of the exchange reaction with liquid and gaseous water (7, 81, 83, 85, 86) is still an open problem.

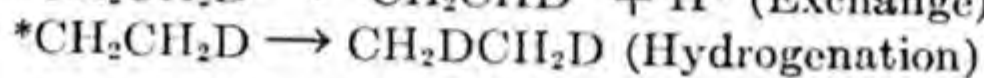
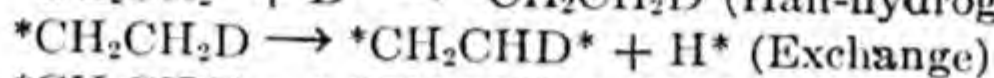
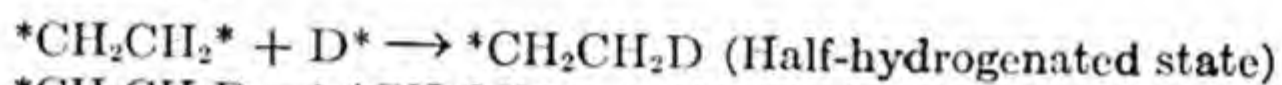
The notion that a saturated hydride RH , when it is chemisorbed, is held as R and H fragments seems fundamentally sound. So far as the present author is aware, an appreciable parahydrogen conversion is always obtained in such cases, showing the presence of chemisorbed hydrogen. This is in direct contrast to chemisorbed ethylene and carbon monoxide (see

below), where the parahydrogen conversion may be almost completely inhibited.

VIII. EXCHANGE AND HYDROGENATION OF UNSATURATED HYDROCARBONS

The hydrogenation of ethylene by deuterium was shown to be accompanied by an atomic exchange (79), and a similar exchange reaction was found with benzene (87). At present three viewpoints may be distinguished

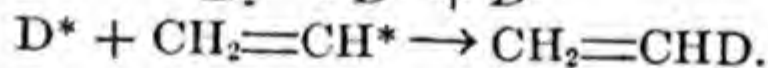
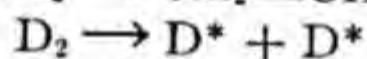
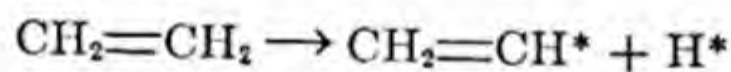
(1) The original viewpoint of Horiuti and Polanyi (88) was that ethylene was adsorbed by the opening of the double bond. Attack by one chemisorbed deuterium atom resulted in a half-hydrogenated state. This could revert to chemisorbed ethylene, losing a hydrogen atom to give heavy ethylene, or attack by a second deuterium atom could result in heavy ethane. On this view exchange and hydrogenation reactions are intimately connected.



The asterisk at each end of the ethylene is meant to indicate the two adsorption bonds, one from each carbon, to two surface metal atoms.

(2) Twigg and Rideal (89) accept the "half-hydrogenated state" as an intermediate in the exchange reaction, only modifying Polanyi's picture in certain details. Hydrogenation is viewed as a separate reaction.

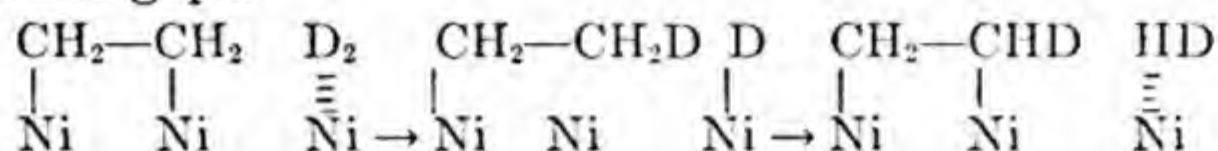
(3) A. Farkas (82) maintains that ethylene, like the saturated hydrides, is adsorbed by rupture of a C—H bond, exchange occurring in the manner mentioned in section VII.



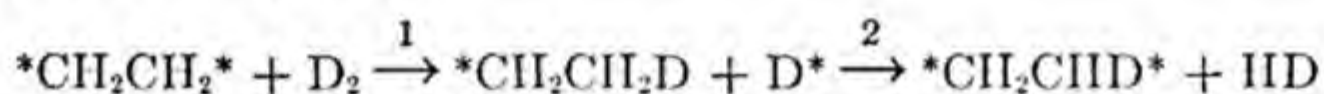
Exchange mechanisms (1) and (2) have been called "associative," and mechanism (3) has been called "dissociative."

In their original paper Polanyi and Horiuti (88) noted that the occurrence of *cis-trans* conversion and double bond migration definitely favored their "dissociative" mechanism for ethylene adsorption. The extensive work of Twigg and Rideal which will now be described has borne out their conclusion. In the first place (89) they made a careful study of the kinetics of the exchange between deuterium and ethylene on a nickel catalyst. Taylor and coworkers had shown that on a specially active nickel catalyst this exchange was detectable at -80°C . (90), while the exchange with ethane only set in at 100°C . (80). Twigg and Rideal found that in the presence of ethylene the $\text{H}_2 + \text{D}_2$ reaction was completely inhibited at temperatures up to 160°C ., pointing to an absence of chemisorbed deu-

terium atoms. At 156° C. the exchange and hydrogenation rates were both independent of ethylene pressure and directly proportional to deuterium pressure. These results thus point to a very strong chemisorption of ethylene by opening of the double bond. Since the ethylene is assumed to be adsorbed at two points, it follows that there will be gaps in the monolayer, and they suppose that the exchange involves deuterium molecules adsorbed on these gaps.

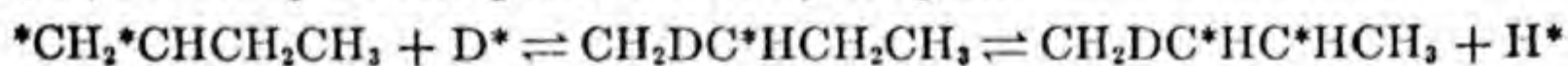


Or in our shorthand notation



The apparent activation energy of 18.6 kcal. was attributed to step 1 or 2, the adsorption or desorption of deuterium. A chemisorbed atom, D^* , is believed to exchange very rapidly with hydrogen atoms in neighboring ethylene molecules. According to this view a deuterium molecule following the initial act of adsorption will come to equilibrium with six neighboring CH_2 groups before desorption and thus the hydrogen desorbing from the catalyst in the initial stages of reaction should contain 14% deuterium. They found 20% deuterium, in reasonable agreement with calculation.

Conn and Twigg (91) found that no exchange occurred between ethylene and ethylene- d_4 on a nickel catalyst. Twigg (92) further showed that double bond migration in the case butene I \rightarrow butene II occurred on his nickel catalyst, but only in the presence of hydrogen.

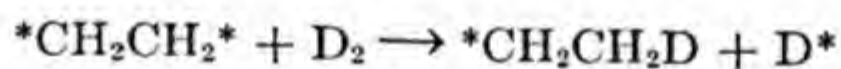


On the dissociative mechanism it would reasonably be expected that only hydrogen atoms which are dissociated at the relatively low temperature of experiment, i.e., those adjacent to the double bond, would exchange with deuterium. Twigg (93) found, however, that all the hydrogen atoms in propylene and butylene were exchangeable, as may be understood by consideration of the associative mechanism for double bond migration above.

Using data on bond lengths and bond angles, Twigg and Rideal (94) calculated that a spacing of 2.73 Å. would be just right to give two point adsorption of the $-\text{CH}_2\text{CH}_2-$ biradical. The active catalysts have spacings in the neighborhood of this value. They showed that while ethylene molecules could pack so as to fill the nickel surface and exclude chemisorbed hydrogen, the bulky nature of the methyl ethylenes would necessarily result in bare sites which could chemisorb hydrogen. In agreement with their calculation, they found that an $\text{H}_2 + \text{D}_2$ reaction took place in the presence of the substituted ethylenes.

This extensive work finds a natural explanation in terms of the associative mechanism, though A. Farkas has offered interpretations of some of the results in terms of his dissociative mechanism. He suggested (95) that the absence of exchange in ethylene-ethylene- d_4 was due to a low concentration of chemisorbed hydrogen. He has also proposed a mechanism for double bond migration (82). His remarks, particularly on double-bond migration, have been criticized by Twigg (96), who has also pointed out the necessary critical experiment. If ethylene is adsorbed in the way Farkas suggested, hydrogen should desorb and be detectable in the gas phase. This experiment has not yet been made.

There are some grounds for regarding hydrogenation as a separate problem, and its mechanism is still obscure. A. Farkas (82) has shown that in the catalytic hydrogenation of acetylenic or ethylenic bonds the products formed are not necessarily those of the highest thermodynamical stability, but those which would result from *cis*-addition of the hydrogen. He concluded that hydrogen atoms are *not* added independently, but that both the hydrogen atoms are added more or less simultaneously from one molecule. This argument would not seem to be valid, and Greenhalgh and Polanyi (97) have shown how the independent addition of hydrogen atoms to the $-CH_2CH_2-$ biradical, via the half-hydrogenated state, would also give *cis*-addition. Twigg and Rideal (89) found that the activation energy for hydrogenation of ethylene was always 4–5 kcal. less than that for the exchange reaction. Since exchange is limited by the adsorption or desorption process, e.g.,



they supposed the hydrogenation rate to be limited by the addition of molecular hydrogen across the double bond. They showed that the well-known decrease in the temperature coefficient for the hydrogenation was paralleled by a similar effect for the exchange reaction. The decrease sets in at 100° C., which is the temperature at which the desorption of hydrogen commences.

Greenhalgh, Horrex, and Polanyi (97, 98) maintained Polanyi's original view that the half-hydrogenated state, $*CH_2CH_3$, is a half-way house to ethane, reached by the independent attachment of a second chemisorbed hydrogen atom. On their view they consider that the apparent order of the exchange reaction should be one-half that for the hydrogenation, and find this is so for a number of experiments with benzene. Their papers should be consulted for the detailed treatment of a large number of results on the parahydrogen conversion, exchange, and hydrogenation. They predicted that the partial hydrogenation of methyl oleate with deuterium should result in isomers with shifted double bonds, all such isomers containing an atom of deuterium. Baxendale and Warhurst (99a) actually

found the main product of this experiment to be light elaidic acid. While obtaining no positive evidence, they considered that their result is at least reconcilable with the associative mechanism, and is definitely against the dissociative mechanism.

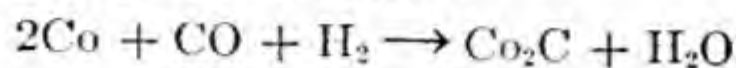
Balandin (99b) in a recent paper assumes that hydrogen and the substrate are adsorbed on two different kinds of site. Exchange and hydrogenation are limited in rate by the formation of the half-hydrogenated state, through the migration of a hydrogen atom between the two kinds of center. He discusses in detail published kinetic data from this point of view.

O. Beeck (33d) gives a short account of his extensive investigations on the hydrogenation of ethylene on evaporated films of metal, particularly nickel. We can only make tentative comments on this work, since full details have still to appear, and a monograph is in preparation by Beeck and Wheeler. Beeck's values for the heats of chemisorption for hydrogen on nickel are 30–18 kcal., and for ethylene 60–25 kcal., the heats decreasing with surface covering. These figures would support the Twigg-Rideal view that a nickel surface exposed to a mixture of ethylene and hydrogen is largely covered by chemisorbed ethylene, and indeed it would seem quite possible to reconcile Beeck's kinetic data on the hydrogenation with this view. However, Beeck takes quite a different line. He has obtained evidence that ethylene is largely adsorbed as acetylenic complexes. These block the surface and in his view limit the rate of reaction, which is determined by the amount of hydrogen chemisorbed on the fraction not covered by acetylenic complexes. Experimentally he finds that ethylene will pick off hydrogen atoms from a preadsorbed film very rapidly, and he thus considers that reaction occurs by collision of ethylene from the gas phase with the chemisorbed hydrogen. At first sight, this view would conflict with Twigg and Rideal's observation on the inhibition of the $H_2 + D_2$ reaction, but further discussion at present would be premature. Besides these conclusions on the kinetics of the reaction, which are undoubtedly controversial, Beeck presents interesting data on the relative efficiencies of the various transition metals. Rhodium turns out to be the best catalyst, which he associates with its 3.75 Å. spacing.

IX. THE FISCHER-TROPSCH SYNTHESIS

This provides an interesting example of the diagnostic value of the parahydrogen conversion. In the normal synthesis carbon monoxide and hydrogen are passed over a promoted iron or cobalt catalyst at atmospheric pressure and 200–250° C., long chain hydrocarbons being formed. Under these conditions Craxford (100) found the parahydrogen conversion to be

inhibited. Thus there is little chemisorbed hydrogen on the catalyst and Craxford gave reasons for supposing, in the first instance, that a cobalt carbide surface is formed by the reaction

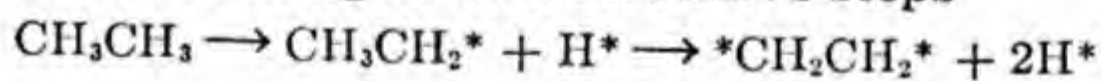


The carbon atoms are then reduced to CH_2 groups which polymerize to long chains, and are broken off the surface by the attack of the rather scarce chemisorbed hydrogen atoms. When, however, the rate of carbide formation is low, there is an appreciable concentration of chemisorbed hydrogen and the CH_2 groups have no chance to polymerize but are hydrogenated to methane. Thus, a catalyst producing methane is also found to give the parahydrogen conversion.

Herington (101) considered the CH_2 groups are held on the short spacings of the catalyst, as had been postulated already for ethylene (94). Thus, ethylene added to the synthesis gas is incorporated in the oil products. On the other hand, acetylene is probably held by two point contact on the long (3.5 Å.) spacing, and then polymerizes independently of the Fischer-Tropsch synthesis.

X. DEHYDROGENATION

As was pointed out earlier, the mechanism of hydrogenation is still obscure, and since there has been little work in recent years on dehydrogenation, we can only discuss possible mechanisms in the most general way. The reaction is normally conducted at sufficiently high temperatures to assume chemisorption of the substrate, e.g., ethane, by rupture of the C—H bond. We would imagine two successive steps



At temperatures of 400° C. or so, the desorption of ethylene and hydrogen will proceed fairly rapidly on most catalysts. There would seem no reason to postulate simultaneous release of two hydrogen atoms to form a molecule, i.e., the reverse of the hydrogenation mechanism, since conditions in the chemisorbed layer will be different from those Twigg and Rideal found for the hydrogenation at 100° C. Since chemisorbed hydrogen is expected, bond migration will probably occur simultaneously.

Certain classical work is in accordance with this view. Thus Palmer and Constable (102) showed that the five alcohols, ethyl, propyl, butyl, isobutyl, and isoamyl, had the same rates of dehydrogenation on a copper catalyst under the same conditions. The energy of activation was about 22 kcal. They supposed that the alcohols were adsorbed with their chains vertical to the catalyst surface, and that the rate determining step was the removal of a hydrogen atom from the hydroxyl group (103). The rearrange-

ment of bonds then expelled the second hydrogen atom from the carbon atom without activation energy. We would, however, imagine that the second step would be adsorption at the carbon atom with rupture of a carbon-hydrogen bond, though the activation energy for this second step might be small. Balandin (104) has considered that two point contact is necessary in the dehydrogenation of ethyl alcohol, this condition defining the necessary lattice spacing in the catalyst (105). His view again is in agreement with the above picture, if we suppose that the contact at two points does not need to occur simultaneously.

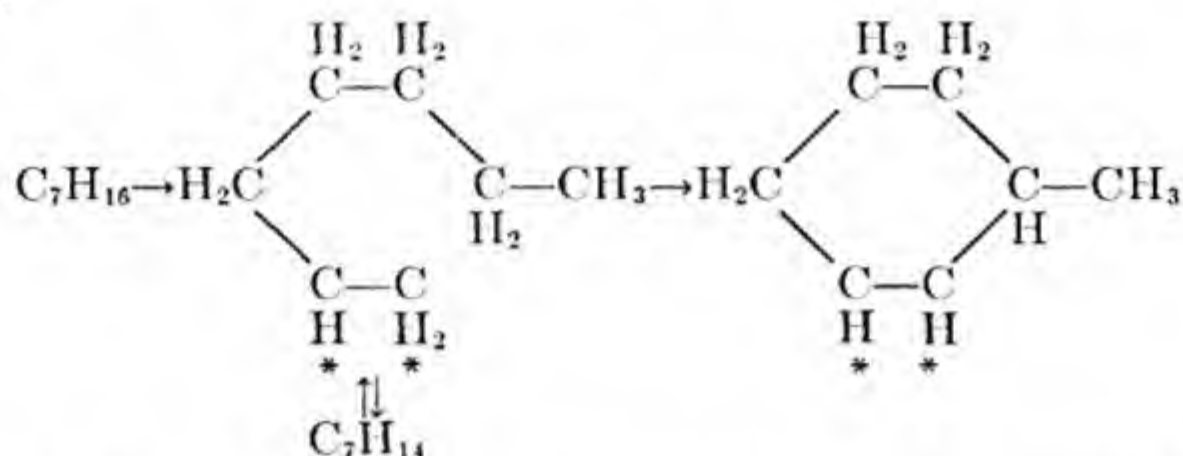
Schwab (106) has examined the dehydrogenation of formic acid on metal alloy catalysts, paying particular attention to homogeneous solutions (α phases) of silver with other metals. Except where the second metal was itself an active catalyst (platinum, palladium, gold), the added metal increased the activation energy of the dehydrogenation process, the increase being greater the greater the valency of the added metal. More specifically, the increase in activation energy was related to Hume-Rothery's electron concentration function for the solute metal, i.e., the number of valency electrons divided by the number of atoms. Thus, as the Brillouin zone of the alloy fills up with electrons, the activation energy increases. Additional support came from considering the complete series of phases formed as one metal, for example antimony, was added to silver. According to H. Jones, as the Brillouin zone becomes filled with electrons the phase becomes unstable. At the phase change a new lattice is formed, with a more capacious zone to accommodate further electrons. Schwab shows that the phase change is accompanied by a fall in activation energy for the alloy as a catalyst. His conclusion is that the primary step in the catalysis is the loss of two electrons to the Brillouin zone of the metal, the two hydrogen ions left subsequently slipping into interlattice places near the metal surface.

XI. CYCLIZATION OF *n*-PARAFFINS

In the presence of oxide catalysts such as chromium oxide at 500°C., *n*-heptane will cyclize to toluene. There are also many other possible reactions, and Taylor and Turkevich (107) have examined the thermodynamics of the reaction and its alternatives. They concluded that cyclization was the favored reaction above 300°C., and pointed out the need to choose a catalyst which activated the C—H rather than the C—C bond.

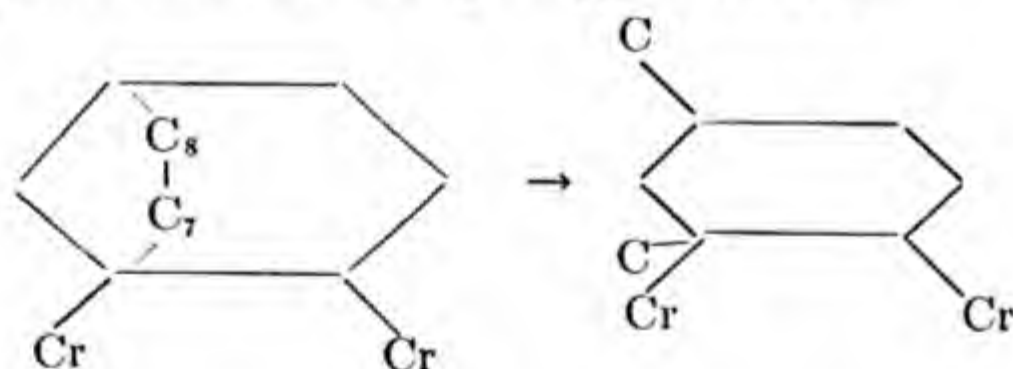
Pitkethly and Steiner (108) reacted *n*-heptane on a dehydrogenating catalyst in the presence of hydrogen at 475°C. For a constant contact time they found a constant heptene to heptane ratio in the products, when the partial pressure of hydrogen was varied from 120 to 495 mm. mercury.

Increased contact time sent up the yield of toluene, but left the heptene yield unchanged. These results suggested to them that heptene was an intermediate in the production of toluene and was present in a stationary concentration.



The methyl cyclohexene is subsequently dehydrogenated to toluene.

Herington and Rideal (109) consider that the intermediate heptene is held by two point contact at the double bond, as in the above formulas. The double bond may migrate to a favorable position for ring closure to occur. They investigated molybdenum oxide as catalyst. They associated the catalytic activity with a 2.79 Å. spacing of the molybdenum atoms not present in the metal itself, and this enabled them to make a simple statistical calculation of the variation of total yield of aromatics with the nature of the paraffin feed, in agreement with experiment. Their failure to calculate the distribution of the different aromatics they attributed to isomerization on the catalyst. *m*-Xylene and *p*-xylene, for example, were found in the products from *n*-octane, and these could only arise by an isomerization accompanying the actual ring closure. They supposed this to involve the formation and rupture of a subsidiary ring, as below.



XII. THE HYDROGEN-OXYGEN REACTION

While this reaction was one of the first to be investigated, its mechanism is still obscure. Benton and Elgin (110) found for a silver catalyst that the reaction rate was independent of the oxygen pressure and directly proportional to the hydrogen pressure. These kinetics fitted in with their adsorption measurements, which showed zero adsorption of hydrogen but an appreciable adsorption of oxygen. They supposed that gaseous hydrogen molecules attacked the adsorbed oxygen, and to account for the slow rate observed, suggested that only oxygen atoms next to bare spaces could react.

Such a picture would fall in with the general viewpoint taken in this paper. However, while gold (111) showed a similar adsorption behavior, the reaction rate was proportional to the square of the hydrogen pressure and directly to the oxygen pressure.

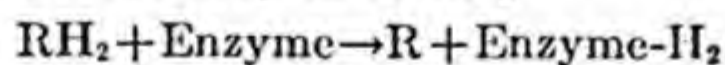
Again, investigations of nickel (112), silver (113) and platinum (114) in Chapman's laboratory have emphasized that the chemisorbed film is mainly oxygen, and the view has been expressed that the reaction goes through an alternate oxidation and reduction of the surface.

The complex nature of these reactions may, in part, reside in the tendency for certain metals to give surface oxide layers several molecules thick which may, or may not, be catalysts for the reaction. Thus, while silver or gold is poisoned by a thick oxide layer (115), this does not seem to be the case for nickel (112), which, in the presence of a hydrogen-oxygen mixture, is reported to be covered by an oxide film 20 Å. thick. Bulk nickel oxide is known to be a catalyst (116).

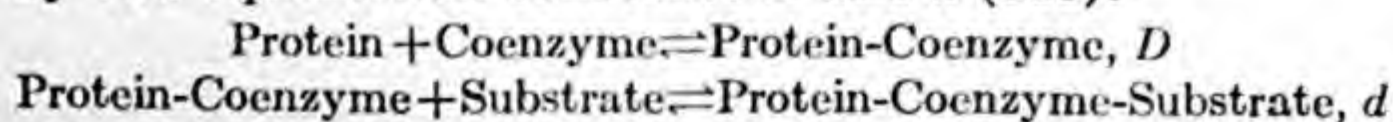
XIII. BIOLOGICAL ACTIVATION OF HYDROGEN

The biological activation of hydrogen in organic compounds, forming, as it does, the first step in biological oxidations, is a vast field, which we cannot attempt to review here. The few remarks that follow are only intended to relate this field to the activation of hydrogen by metals, as it is quite likely that there is a common basis for catalytic activity in the two cases.

H. Wieland (117) showed that dehydrogenation was the first stage in the enzymatic oxidation of organic molecules. Thus, palladium black catalyzed the oxidation of ethyl alcohol not only by oxygen but also anaerobically by quinone or methylene blue. The palladium black could be replaced by dehydrogenases, and the first step is clearly



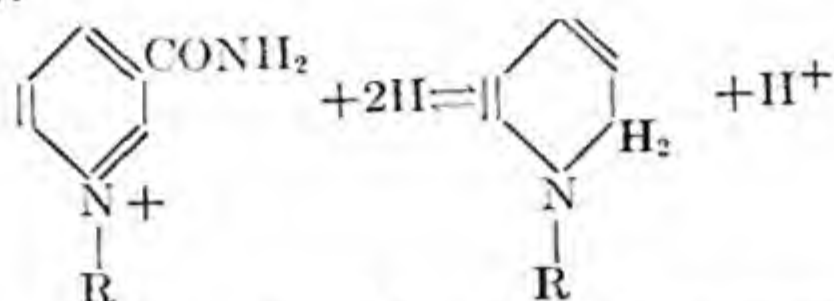
It is now known that the enzyme may be separated by dialysis into a coenzyme and a protein. The protein is the true catalyst and is specific for each substrate. Its function is to combine with both substrate and coenzyme, when it can mobilize the hydrogen for transfer from the one to the other. The combinations are supposedly reversible, and have been described by two equilibrium constants D and d (118).



A first order velocity constant, k , served to describe the actual hydrogen transfer within the complex.

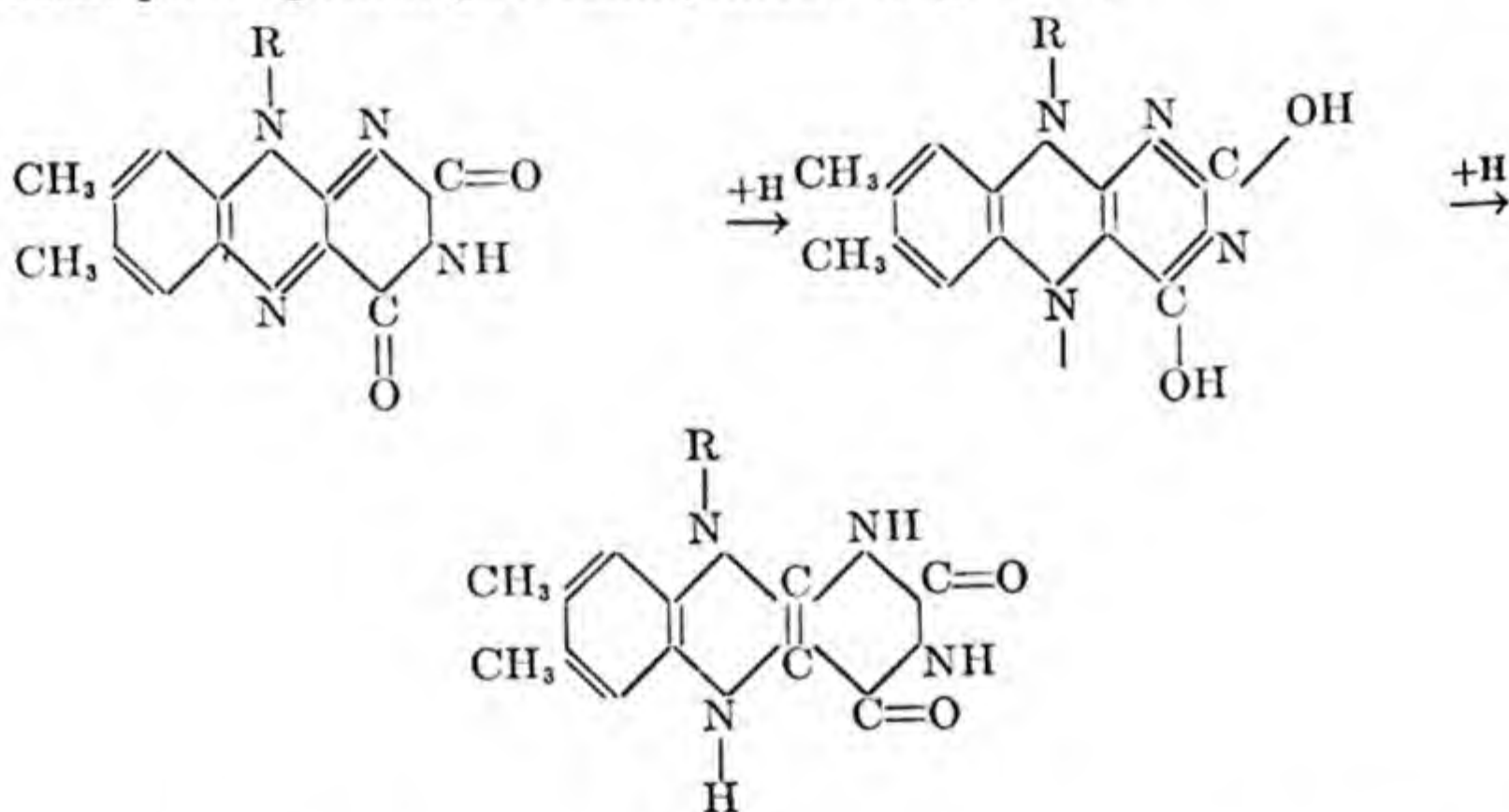
Two coenzymes have been isolated and their structures determined.

Coenzyme I (cozymase) acts with alcohol and some other substrates, while coenzyme II acts with glucose 6 phosphate. They are both phosphopyridine nucleotides (119), the active group in hydrogen transfer being the pyridinium ring (120).



D , d , and k have been determined by Warburg from an analysis of the kinetics of the reaction.

The hydrogen is next transferred to the cytochrome reductase molecule, the prosthetic group of which is alloxazine (121). In this case there is definite evidence that the two hydrogen atoms are added separately, the alloxazine passing through a semiquinone stage (122).



Michaelis and Schubert (123) have represented dehydrogenation as a removal, independently, of electron plus hydrogen ion, rather than hydrogen atom. While this concept is no doubt physically exact for ionizable compounds like hydroquinone, it would seem to have a purely formal use for substrates such as succinic acid, where the hydrogen atoms concerned do not ionize. The concept, however, serves a useful purpose in unifying the dehydrogenase action with the oxygen end of the enzyme chain, where the redox changes are simple electron transfers between the iron containing cytochrome molecules.

Two enzymes are found in certain bacteria, such as *Escherichia coli*, which will activate gaseous molecular hydrogen (124). Both have been shown to catalyze forward and back reactions. Hydrogenase catalyzes $\text{H}_2 + \text{A} \rightleftharpoons \text{AH}_2$, where A is an acceptor such as methyl viologen, or even a

one-carbon compound. Hydrogenlyase catalyzes the production of formic acid, $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{HCOOH}$. *E. coli* has also been shown to catalyze the exchange of atoms between deuterium and water (125, 126).

Huberman and Rittenberg (126a) find that *Proteus vulgaris* contains an enzyme that catalyzes the exchange reaction $\text{H}_2 + \text{D}_2$. The enzyme is inhibited by CO and HCN and they tentatively conclude that it is a ferrous heme system.

XIV. GENERAL CONCLUSIONS

We are scarcely at a stage where any generally applicable theories of either the kinetics or the energetics of catalysis may be applied with any real confidence. As the present author sees it, the need is still for thorough studies of specific systems, using combinations of chemical and physical techniques. Little advantage has been taken of the methods which Langmuir made available 30 years ago for the detailed study of catalytic reactions under clearly defined conditions, and the tendency has been to work with complex surfaces, where "active spots" may be expected to play an important role. This notion of "active spots" must remain a relatively sterile hypothesis until the characteristics of uniform surfaces have been more fully explored. With further data of this kind at our disposal we could more confidently approach the problems presented by the physical (127) or chemical (128) heterogeneities of activated "industrial" catalysts. So the remarks in this section may only be regarded as the personal orientation of the author to what is still a predominantly experimental field of research.

1. Stability of the Chemisorbed Film

It is now clear from Roberts' work that chemisorbed films of hydrogen and other gases may be much more stable than was generally supposed. They may still, however, be very reactive, so that suggestions (129) that catalytically active hydrogen is *weakly* chemisorbed cannot be generally applicable. It seems clear also that the Langmuir-Hinshelwood picture (3) of catalysis in a simple competitively occupied chemisorbed layer must be modified in such cases. The Rideal picture (2) of interaction between a van der Waals layer and a chemisorbed layer has so far been applied with some success to a number of reactions, and probably has a fairly wide application to reactions at relatively low temperatures. The domain of the Langmuir-Hinshelwood picture would seem to be reactions at relatively high temperatures, where desorption of the chemisorbed layer has set in.

2. Geometry of the Catalyst Surface

Roberts has shown on theoretical grounds how gaps may arise in immobile and mobile monolayers. While much remains to be done in the experi-

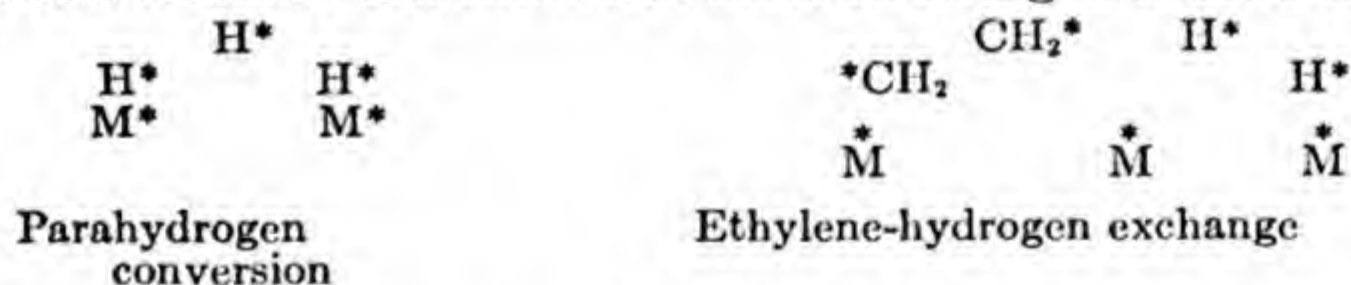
mental investigation of these gaps, the concept would seem to be of the greatest importance for catalysis. Herington and Rideal (130) have shown how the action of bulky poisoning molecules in excluding the occupation of neighbor sites in a uniform lattice can give rise to nonlinear poisoning curves which have previously been explained on the active spot theory. Some success has also been achieved with the notion that the spacings in a lattice active in the catalysis of ethylene and acetylene are those which can chemisorb the biradical. In this connection the experimental work of Beeck and coworkers (9) is of the greatest importance. They showed how oriented metallic films could be prepared by evaporation from wires in the presence of inert gas and demonstrated in this way that the 110-plane of nickel was more active in the hydrogenation of ethylene than the other planes. A great deal more work along this line is required before we can get a clear picture. The work would suggest that even an aged wire might exhibit more than one zone of activity, depending on the occurrence of more than one lattice plane in the surface.

3. *Energetics of the Transition State*

A catalyzed reaction follows a path of relatively low free energy of activation, in the sense of Eyring's theory, as compared with the same reaction proceeding without a catalyst. Where a comparison is possible, it would seem that inorganic catalysts lower the energy (heat content change) of activation (3), and the same holds for enzymes (131). The effect of catalysts on the entropy of activation, so far as the present author is aware, is, in general, less marked. In some way the molecules adsorbed on the metal, metal oxide, or other catalysts, or held to a specific protein, are converted into a more labile form, i.e., the potential hill for one specific mode of reaction (out of perhaps a number of such) is considerably lowered.

It has long been known that mere adsorption is not sufficient. Indeed, tungsten adsorbs ethylene very strongly and possesses just the right 2.73 Å. spacing to hold it in the biradical form, yet it does not seem to be an efficient catalyst for the exchange reaction between hydrogen and ethylene (28). In the enzyme field Quastel (132) has shown how a dehydrogenase is inhibited if molecules of related structure to the specific substrate are added to the system. These molecules are, indeed, adsorbed by the enzyme, or perhaps more correctly, form the enzyme-substrate complex, because this is largely a stereochemical matter. They are not, however, brought into reaction. Thus various acids containing the CH_2COOH group, such as malonic and glutaric acids, will inhibit the dehydrogenation of succinic acid.

It is not clear how far all catalysts, metals, metal oxides, and proteins may possess a common basis for their activity, but it seems reasonable to take this view as a working hypothesis for the present. Stearn (131), for example, has supposed that the charged groups present in proteins lower potential barriers for adsorbed substances by increasing the ratio of coulombic to exchange energy in the bonds concerned. Such an effect follows from the London-Eyring-Polanyi treatment of potential energy barriers. Again, we have referred to Polanyi's notion (77) concerning the effect of resonance energy in depressing the activation energy for a reaction. This idea has so far only been developed for the diene synthesis (133), and it can scarcely be applied to catalysis until we possess a more detailed picture of at least one reaction path, which is a matter for experiment. Theoretically, too, we need to know more about the energy levels and wave functions of the surface electronic states. All three types of catalyst possess common energy levels, i.e., the valency electrons of the atoms are not localized but may move through the lattice (excitation energy being necessary for nonmetals). Metals are electronic conductors, and certain of the catalytic oxides, e.g., nickel oxide, are known semiconductors. Szent Györgyi (134) has recently shown that gelatin impregnated with a dye is a photoconductor. It is not, indeed, an easy matter to formulate the problem in any but a vague way by the electron pair method of Pauling. The whole problem of transition states adsorbed on metals is probably better considered in terms of the molecular orbital method of Lennard-Jones and Coulson (135) and others, since this method is closely related to the method used for metals. A virtue of the gap hypothesis for catalysis is that we can visualize the transition state as a ring of mobile electrons.



M indicates a surface atom of the metal and the asterisk a mobile electron. The resonance energy might be expected to strongly depress the energy of formation of such a complex from the initial adsorbed reactants, i.e., the activation energy for the reaction. Considerations of this kind, however, still fall into the realm of speculation.

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Isomerization of Alkanes

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I. INTRODUCTION

The isomerization of *n*-butane and higher alkanes has assumed great importance in the last 10–15 years. The need for isobutane as a charging stock for alkylation processes and the necessity for converting low octane number straight chain hydrocarbons to their higher octane number branched chain isomers, gave an impetus to the study of isomerization of alkanes.

The most important catalysts found for this reaction are aluminum chloride and aluminum bromide. The early investigators reported that these aluminum halides are catalysts for the isomerization of *n*-butane to isobutane; later investigators found, however, that the reaction proceeds only when traces of water or hydrogen halide are used in conjunction therewith. More recent work indicated that under certain controlled conditions, even aluminum halides-hydrogen halides do not catalyze the isomerization of butanes unless traces of olefins or their equivalent are present.

The isomerization of liquid paraffins such as pentane and hexane proceeds also in the presence of aluminum halides-hydrogen halides. This isomerization, however, is always accompanied by decomposition. It was found that the decomposition can be inhibited by the presence of various substances such as hydrogen, cyclohexane, aromatic mono- and polynuclear hydrocarbons, isobutane, etc. In the case of heptanes and higher molecular weight alkanes the use of hydrogen was not successful in inhibiting the cracking reaction.

Various other catalysts such as sulfuric acid, molybdenum oxide, etc., also have been investigated for the isomerization of alkanes. The isomerization in the presence of the oxide catalysts proceeds usually at high temperatures and in the presence of hydrogen. These catalysts have no significant importance. Sulfuric acid is not a general isomerization catalyst; it was successfully used in only a few isolated cases such as in the isomerization of 2-methylpentane to 3-methylpentane.

II. ISOMERIZATION OF BUTANES

1. *Early Investigations*

The isomerization of *n*-butane to isobutane and the reverse isomerization proceed in the presence of catalysts containing either aluminum chloride or aluminum bromide; the latter, by virtue of its high solubility in hydrocarbons (Heldman and Thurmond, 1; Boedeker and Oblad, 2) and its higher activity, causes the isomerization of butanes to proceed at lower temperatures.

The early investigators of the isomerization of *n*-butane to isobutane did not take special precautions to purify the reagents used or to carry out the reaction under conditions which would exclude the contact of air, moisture, or other impurities. For this reason the results obtained are not always reproducible.

a. Aluminum Bromide. Both *n*-butane and isobutane were isomerized in a sealed tube at about 27° in the presence of 18.9% by weight of aluminum bromide (Montgomery, McAteer, and Franke, 3). The isomerization proceeded rather slowly, and over two months were required to attain the

equilibrium state (Section II, 3) starting with either of the hydrocarbons.

b. Aluminum Chloride. The early investigators of isomerization of hydrocarbons in the presence of aluminum chloride concluded that aluminum chloride is active as an isomerization catalyst only when used in the presence of hydrogen chloride.

n-Butane at a suitable temperature (Schuit, Hoog, and Verheus, 4) was converted in large yields to isobutane when contacted in an autoclave with aluminum chloride and hydrogen chloride. According to these authors the optimum temperature for isomerization was 100°; when the temperature was decreased, the rate of reaction dropped rapidly, whereas, when the temperature was raised, side reactions became pronounced (Table I).

TABLE I

Effect of Temperature on the Isomerization of Butanes in the Presence of Aluminum Chloride-Hydrogen Chloride

Temp. °C.	Composition of Product			
	Propane %	Isobutane %	<i>n</i> -Butane %	Pentanes and Higher %
20	...	15.0	85.0	...
40	...	17.6	82.4	...
60	...	22.6	77.8	...
80	...	35.1	64.9	...
100	3.8	62.9	29.4	3.9
120	70.5	16.7	10.0	2.8

The apparatus consisted of a 1-l. capacity stainless steel rotating autoclave. The reagents used in each experiment were composed of 80 g. butanes (11% isobutane and 89% *n*-butane), 40 g. aluminum chloride, and 8 g. hydrogen chloride. The duration of each experiment was 4 hours.

2. High Vacuum Technique

The isomerization of butanes using a high vacuum technique for the purification and introduction of the reactants was investigated (Leighton and Heldman, 5). It was found that completely anhydrous aluminum bromide did not act as a catalyst for the isomerization at 85°; the addition, however, of a small amount of hydrogen bromide to the reactants caused *n*-butane to isomerize.

a. Effect of Promoters. The effect of various promoters upon the isomerization of butanes was also investigated (Heldman, 6). The experimental results summarized in Table II show that compounds such as sodium chloride, sodium bromide, boron fluoride, and the bromoparaffins are effective isomerization promoters for aluminum bromide.

b. Effect of Olefins. The isomerization of *n*-butane was studied with highly purified reagents using a high vacuum technique for charging and

discharging the products (Pines and Wackher, 7). It was found that the isomerization of *n*-butane under relatively mild conditions did not proceed when catalyzed in the presence of either aluminum chloride-hydrogen chloride or aluminum bromide-hydrogen bromide. In order to cause such

TABLE II

The Effect of Promoters upon the Isomerization of n-Butane in the Presence of Aluminum Bromide

Temp. °C.	Time, hrs.	AlBr ₃ , Moles/100 moles <i>n</i> -butane	Promoter		Analysis % isobutane
			Kind	Moles/100 moles <i>n</i> -butane	
25	96	10.4	HBr	13.5	14
25	72	29.5	HBr	7.6	17
25	149	3.7	HBr	4.0	38
84 ± 2	12	2.9	HBr	0.7	8
84 ± 2	12	2.4	HBr	1.7	15
84 ± 2	58.7	29.6	HCl	1.4	59
84 ± 2	44.4	6.5	HCl	5.2	>69
25	96	17.1	NaBr	20.7	0.4
25 ± 3	286	6.1	NaBr	6.1	10
50 ± 1	48	4.0	NaBr	5.8	1.3
84 ± 2	59	1.6	NaBr	3.5	5
84 ± 2	44	3.0	NaBr	10.2	12
25	96	34.7	NaCl	18.8	0.5
84 ± 2	44	3.3	NaCl	5.3	38-40
84 ± 2	35	2.8	NaCl	8.1	31-36
25	95	15.6	BF ₃	1.8	>45
84 ± 2	59	1.3	BF ₃	5.0	20
84 ± 2	44	2.8	BF ₃	10.6	42
25	96	10.6	CH ₃ Br	16.0	11
25 + 3	405	7.6	CH ₂ Br ₂	60.0	75
84 + 2	12	17.5	<i>n</i> -C ₄ H ₉ Br	6.1	36

isomerization it was necessary to add various compounds which are ordinarily present as impurities in the commercial butane isomerization. The addition of 0.01% butenes to *n*-butane was sufficient to cause isomerization in the presence of aluminum chloride-hydrogen chloride at 100°. In the absence of olefins aluminum halide-hydrogen halide did not cause the isomerization of *n*-butane, unless the experimental conditions were conducive to the formation of decomposition products. This was accomplished either by raising the temperature of reaction or by increasing the

concentration of hydrogen halide. The data obtained by these authors were not in agreement with the experimental results described previously (Leighton and Heldman, 5) in which the butane probably was not purified sufficiently to remove components which might have acted as initiators for the isomerization.

(1) Aluminum bromide-hydrogen bromide. The effect of olefins upon the isomerization of *n*-butane catalyzed by aluminum bromide-hydrogen bromide is summarized in Table III.

TABLE III

*Effect of Olefins upon the Isomerization of n-Butane
Catalyzed by Aluminum Bromide-Hydrogen Bromide*

Experiment No.	1	2	3	4
Mole % butenes in <i>n</i> -butane	0	0.03	0.08	0.58
Isobutane produced, %	0.2	2.1	19.3	65.6

Temperature of isomerization: $25 \pm 0.1^\circ \text{C}$. Duration of each experiment: 15 hours. Molal ratio of reagents used: *n*-butane/aluminum bromide/hydrogen bromide = 100/9.3/2.3.

The table shows that the addition of 3 parts butenes per 10,000 parts *n*-butane is sufficient to start the isomerization, while in the presence of 5.8 parts olefins per 1000 parts *n*-butane the yield of isobutane formed was very large.

(2) Aluminum chloride-hydrogen chloride. Table IV represents the

TABLE IV

*Effect of Olefins upon the Isomerization of n-Butane Catalyzed
by Aluminum Chloride-Hydrogen Chloride*

Experiment No.	1	2	3	4	5	6
Mole % butenes in <i>n</i> -butane	0	0.013	0.05	0.09	0.28	2.49
Composition of the hydrocarbon layer after reaction, mole %						
<i>n</i> -Butane	99.9	87.6	87.0	82.8	72.3	44.9
Isobutane	<0.1	11.8	12.6	16.9	26.8	51.0
Pentanes and higher	0.1	0.6	0.4	0.3	0.9	3.9
Isobutane in the butane fraction, mole %	0	11.9	12.7	17.0	27.0	53.2

The molal equivalents of reagents used in each experiment: *n*-butane, 100 moles; aluminum chloride, 5.9 moles; hydrogen chloride, 3.1 moles. The experiments were made by heating the reagents in sealed tubes for 12 hours at 100° .

results obtained from the study of the effect of olefins upon the isomerization of *n*-butane catalyzed by aluminum chloride-hydrogen chloride. The reaction was carried out by heating *n*-butane, aluminum chloride, and hydrogen chloride in a sealed tube at 100° for 12 hours; the respective molal concentration of these reagents was 100/5.9/3.1. The concentration of butenes based on the charged butane varied from 0 to 2.6 mole %.

It was found (Pines and Wackher, 7) that aluminum chloride-hydrogen chloride did not cause the isomerization of *n*-butane to isobutane at 100°. The presence however of 1 part butenes per 10,000 parts *n*-butane was sufficient to cause the isomerization. When the concentration of butenes was increased to 2.5% side reactions occurred, as evidenced by the formation of higher hydrocarbons and a small amount of a viscous dark layer; the latter was produced by a complex formation between the catalyst and unsaturated hydrocarbons.

(a) Effect of temperature. The isomerization of *n*-butane proceeded also in the absence of added olefins when the temperature of the reaction was high enough. This was probably due to the fact that at higher temperatures aluminum chloride-hydrogen chloride acted also as a cracking catalyst, causing a partial decomposition of *n*-butane. The product of decomposition served as a promoter for the isomerization of *n*-butane to isobutane. The degree of isomerization, however, was greater when olefins were added. The experimental data are given in Table V.

TABLE V

The Effect of Temperature upon the Isomerization of n-Butane Catalyzed by Aluminum Chloride-Hydrogen Chloride

Experiment No.	1	2	3	4	5
Temp., °C.	100	125	150	100	125
Reagents used: moles per 100 moles <i>n</i> -butane					
Aluminum chloride	8.91	9.26	9.50	9.21	9.14
Hydrogen chloride	5.87	3.24	3.19	5.86	3.37
Butenes	0.09	0.101
Analyses, mole %					
Propane	...	0	3.3	0	0
Isobutane	0.1	16.3	62.4	16.9	22.2
<i>n</i> -Butane	99.8	83.1	31.8	82.8	76.9
Pentanes	0.1	0.6	2.5	0.3	0.9
HCl recovered, mole %	98	95	97

(b) Effect of hydrogen chloride. The isomerization of *n*-butane proceeded also in the absence of added olefins when the hydrogen chloride

concentration was increased from about 6 to 18 mole %, as shown in experiments 1 and 2 of Table VI. At more elevated temperatures, such as 150°, the concentration of hydrogen chloride had a pronounced effect upon the course of reaction of *n*-butane. In the presence of 3 mole % of hydrogen chloride, isomerization was the principal reaction, while in the presence of 7% hydrogen chloride, cracking occurred predominantly.

TABLE VI

*Effect of Hydrogen Chloride Concentration
upon the Isomerization of n-Butane*

Experiment No.	1	2	3	4	5
Temp., °C.	100	100	150	150	150
Reagents used: moles per 100 moles of butane:					
Aluminum chloride	8.91	8.84	9.18	9.50	9.05
Hydrogen chloride	5.87	17.6	0	3.19	7.12
Analyses, mole %					
Propane	3.3	57.9
Isobutane	0.1	14.1	11.1	62.4	23.4
<i>n</i> -Butane	99.9	85.0	88.2	31.8	13.8
Pentanes and higher	0.1	0.9	0.7	2.5	4.4
HCl recovered, mole %	98	97	57

c. Effect of Oxygen. Since air is one of the constituents which might be present as an impurity during the isomerization of butanes, the effect of small amounts of oxygen upon the course of isomerization was investigated (Pines and Wackher, 8). The catalyst used for this reaction was either aluminum chloride or aluminum bromide. The former, only slightly soluble in the hydrocarbons, was deposited on charcoal in some experiments in order to increase the active surface of the catalyst.

(1) Aluminum bromide. When aluminum bromide was used as a catalyst in the absence of air, *n*-butane did not isomerize even when the solution was exposed to sunlight for 8 hours and then allowed to stand in the dark for an additional 500 hours. The isomerization proceeded, however, when 0.06 mole air per 100 moles *n*-butane was added and the mixture was kept in the dark for 192 hours; the yield of isobutane produced was 7.5%. Nitrogen alone did not cause the isomerization under similar conditions.

The degree of isomerization is a function of the amount of oxygen added and of the length of time the material is exposed to sunlight. After 31 hours of exposure and in the presence of 0.055 mole oxygen, as air, per 100 moles butane, 63.6% isobutane was formed. Sunlight had a beneficial effect upon the rate of isomerization. The experimental results are summarized in Table VII.

A quantitative study was made of the products resulting from the reaction of air with aluminum bromide dissolved in *n*-butane in molal proportions: $C_4H_{10}/AlBr_3/O_2 = 100/9.5/0.30$. It was found that all of the oxygen entered the reaction; the gases which were pumped off, to 10^{-3} mm. of mercury at liquid nitrogen temperature, consisted of 95% nitrogen and

TABLE VII

*Effect of Oxygen upon the Isomerization of n-Butane
in the Presence of Aluminum Bromide at 25°*

Experiment No.	1	2	3	4	5	6	7
Duration of reaction, hrs.							
In dark	500	215	192	22	17	139	102
In sunlight	8	2	4	8	31
Reagents used: moles per 100 moles <i>n</i> -butane							
Aluminum bromide	10.0	12.7	11.0	11.8	11.0	11.1	9.44
Oxygen	0	0.226 ^a	0.06 ^b	0.157	0.06 ^b	0.044 ^b	0.055 ^b
Analyses, mole %							
Isobutane	0	8.7	7.5	15.7	9.5	29.7	63.6
<i>n</i> -Butane	99.5	90.7	91.8	84.3	90.1	59.0	35.0

^a Equal volumes of oxygen and air were introduced.

^b Air was used.

5% paraffinic hydrocarbons. The condensable gases consisted of 63.6% isobutane and 1.4% pentanes, the remainder being *n*-butane. Hydrogen bromide was recovered from the reaction, equivalent to 1.25 moles per mole of oxygen reacted. Part of the catalyst combined with hydrocarbons to form a complex which, after being freed of uncombined aluminum bromide, yielded unsaturated hydrocarbons on hydrolysis. The atomic ratio of bromine to aluminum in the complex was equal to 2.5.

The effect of oxygen upon the isomerization of *n*-butane in the presence of aluminum bromide was also studied in a 1-gallon glass lined steel bomb (Oblad and Gorin, 9). It was found that oxygen is an effective promoter in this type of apparatus also. It was noticed too that oxygen was used up during the reaction. This was in agreement with similar results recorded by others (Pines and Wackher, 8). The isomerization followed a first order reaction with respect to *n*-butane concentration; the reaction rate at a given temperature was largely dependent on aluminum bromide concentration, oxygen concentration, and amount of surface. The rate of oxygen consumption was related to initial oxygen concentration, type of surface present, surface to volume ratio, and aluminum bromide concentration. The aluminum bromide consumption appeared to be related to oxygen consumption.

It was also shown that bromine can be substituted for oxygen as a promoter (Oblad and Gorin, 9).

(2) Aluminum chloride. Isomerization did not take place when *n*-butane was treated with aluminum chloride-charcoal catalyst alone. However, in the presence of a quantity of air such that the concentration of oxygen was approximately 0.01–0.02 moles oxygen per 100 moles *n*-butane introduced, isomerization to isobutane took place. The experimental data are given in Table VIII.

TABLE VIII

*Effect of Oxygen upon the Isomerization
of n-Butane Using Aluminum Chloride as a Catalyst at 25°*

Experiment No.	1	2	3
Duration of reaction, hrs.			
In dark	121	141	0
In sunlight	0	0	16
Agitation	Yes	Yes	No
Reagents used: moles per 100 moles <i>n</i> -butane			
Aluminum chloride, ^a	16.07	17.40	17.05
Oxygen (as air)	0.0168	0.0196	0.0112
Analyses, mole %			
Isobutane	29.9	38.6	7.2
<i>n</i> -Butane	70.1	59.0	91.3
Pentanes and higher	0	2.1	2.1

^a The reaction tubes contained 123 parts by weight of activated coconut charcoal, 10–12 mesh, per 100 parts of aluminum chloride.

d. Effect of Water. The fact that water promotes the isomerization of saturated hydrocarbons when either aluminum chloride or aluminum bromide is used as a catalyst, has been recognized (Nenitzescu and Cantuniari, 10). A vacuum technique was employed in the study of the effect of water upon the isomerization of *n*-butane (Wackher and Pines, 11). Two methods were used for this study: (a) Aluminum bromide or aluminum chloride was treated with various amounts of water, the mixture was heated, and any liberated hydrogen bromide or hydrogen chloride was pumped off. The resulting product, freed of noncombined hydrogen halide, was then used as a catalyst for isomerization of *n*-butane. (b) Aluminum halide, *n*-butane, and water were mixed.

(1) Aluminum bromide. It was found that the amount of hydrogen bromide liberated from the action of water upon aluminum bromide depended upon the molal ratio of water to aluminum bromide used. With the increase of the ratio of the water to aluminum bromide, the amount of hydrogen bromide liberated decreased. The maximum, 1.25 moles hydro-

TABLE IX

Reaction of Aluminum Bromide with Water, and Isomerization of n-Butane in the Presence of the Resulting Reaction Product

		A						
Experiment No.		1	2	3	4	5	6	7
Reaction time: hrs. at 25° C.		70	18	24	45	20	112	47
Reaction time: hrs. at 100° C.		0.75	1.25	1.50	1.25	1.50	0.50	0.50
Charge								
Aluminum bromide, moles		0.00849	0.01026	0.01027	0.0133	0.0121	0.01170	0.01177
Water, moles		0.00856	0.02060	0.03073	0.0532	0.0727	0.04672	0.07040
Moles H ₂ O/mole AlBr ₃		1.01	2.01	2.99	4.01	6.00	3.99	6.00
HBr generated: moles/mole AlBr ₃ reacted		1.25	1.06	0.85	0.69	0.017	0.67	0.017
Unreacted aluminum bromide, moles		0.00103	0.00071	0	0	0	0	0
Unreacted water, moles		0	0	0	0	0.00078	0	0.00061
		B						
Isomerization of n-butane in the presence of the catalyst described in A		20	20	20	20	20	15	12
Reaction time, hrs.		25.0	25.0	25.0	25.0	25.0	80	80
Reaction temp., °C.		0.0935	0.1108	0.1105	0.1428	0.1308	0.1256	0.1266
n-Butane charged, moles		0.01	0.03	0.04	0.01	0	0.23	0
HBr generated, moles/mole AlBr ₃ reacted in A								
Analysis of hydrocarbon product, mole %								
Isobutane		18.7	30.9	16.6	2.7	0.0	62.8	0
n-Butane		81.3	69.0	82.6	96.0	99.0	35.4	100
Pentanes and higher		0	0.1	0.8	1.3	0.1	1.8	0

gen bromide produced per mole aluminum bromide reacted, was formed when the molal ratio of aluminum bromide to water was 1. When the water-aluminum bromide ratio was 2, 3, and 4, the respective amounts of hydrogen bromide produced were 1.1, 0.8, and 0.7 (Table IX, A). By using 6 moles water per mole aluminum bromide aluminum bromide hexahydrate was formed, and therefore no hydrogen bromide was evolved.

The complex resulting from the action of water on aluminum bromide, freed from any noncombined hydrogen bromide, was used as a catalyst for the isomerization of *n*-butane. It was found that by contacting *n*-butane at 25° for 20 hours with the catalysts, isomerization occurred when the molal ratio of water-aluminum bromide was 1, 2, or 3 (Table IX, B). When the ratio was 4, slight isomerization occurred at 25°, but appreciably more occurred at 80°. With a ratio of 6, no isomerization occurred. No appreciable evolution of hydrogen bromide was noticed in these experiments. The results obtained demonstrate that the isomerizing catalyst formed by the action of water on aluminum bromide is not equivalent to an aluminum bromide catalyst, inasmuch as the latter requires hydrogen bromide and traces of olefins to cause the isomerization of *n*-butane.

The effect of water upon the isomerization of *n*-butane that contains aluminum bromide also has been studied. These experiments are not comparable with those described above, as the hydrogen bromide formed was not removed from the reaction zone. It was found that aluminum bromide promoted by water, in spite of the free hydrogen bromide present, is a less active catalyst (Table X) than the corresponding catalyst described

TABLE X

Isomerization of n-Butane in the Presence of Aluminum Bromide and Water

Experiment No.	1	2	3
Duration of reaction, hrs.	20	20	20
Temp., °C.	25	25	25
Charge, moles per 100 moles <i>n</i> -butane:			
Aluminum bromide	9.3	9.3	9.3
Water	9.3	27.9	56.0
Moles H ₂ O/mole AlBr ₃	1	3	6
Hydrogen bromide generated per mole AlBr ₃	0.49	0.48	0.025
Analysis of hydrocarbons, mole %			
Isobutane	13.2	11.8	1.0
<i>n</i> -Butane	86.6	87.1	98.0
Pentanes and higher	0.2	1.1	1.0

in Table IX. In this case, it was again shown that the addition of 6 moles water per mole aluminum bromide had no catalytic activity upon the isomerization of *n*-butane.

(2) Aluminum chloride. The reaction of aluminum chloride with water is, to some extent, similar to the one of aluminum bromide; namely, the more water added, the less hydrogen chloride liberated. With a 1 molal ratio of water to aluminum chloride, 0.71 mole hydrogen chloride was formed; when the water-aluminum chloride ratio was increased to 2, only 0.29 mole hydrogen chloride was generated per mole aluminum chloride reacted (Table XI). The catalysts produced from the action of water on aluminum chloride were less active than those obtained from aluminum bromide and therefore the isomerization experiments were carried out at 80–100°. Unlike aluminum chloride, catalysts produced by the action of water on aluminum chloride did not require the presence of olefins or hydrogen chloride to promote the isomerization of *n*-butane.

TABLE XI

Reaction of Aluminum Chloride with Water and Isomerization of n-Butane in the Presence of the Resulting Reaction Products

A				
Experiment No.	1	2	3	
Duration of reaction, hrs.:				
at 25° C.	460	117	500	
at 100° C.	1	4.5	1	
Charge				
Aluminum chloride, moles	0.0116	0.0113	0.0115	
Water, moles	0.0116	0.0113	0.0230	
Moles H ₂ O/mole AlCl ₃	1.00	1.00	2.00	
Hydrogen chloride generated:				
Moles	0.0082	0.0084	0.0033	
Moles/mole AlCl ₃	0.71	0.74	0.29	
Unreacted aluminum chloride, moles	0	0	0	
Unreacted water, moles	0	0	0	
B				
Isomerization of <i>n</i> -butane in the presence of the catalysts described in A				
Duration of reaction, hrs.	12	12	12	
Temp., °C.	80	100	80	
<i>n</i> -Butane charged, moles	0.125	0.124	0.124	
HCl generated, moles/mole AlCl ₃ used in A	0.24	0.03	0.46	
Analysis of hydrocarbon product, mole %				
Isobutane	9.0	42.3	14.7	
<i>n</i> -Butane	89.7	56.0	84.5	
Pentanes and higher	1.3	1.7	0.8	

Isomerization of *n*-butane in the presence of aluminum chloride and water was also studied. The hydrocarbon and the water were added to the aluminum chloride and the reagents were heated for 12 hours at 100°. The

amount of hydrogen chloride produced in this reaction and the percentage of butane which underwent isomerization decreased with the increase of the molal ratio of water to aluminum chloride used. These experiments confirmed also the observation made previously, that aluminum chloride to which 6 moles of water was added showed no catalytic activity toward isomerization (Table XII).

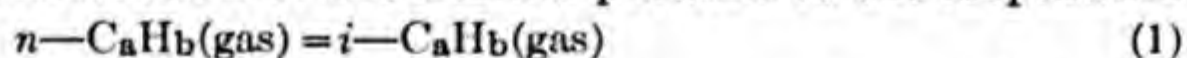
TABLE XII

Isomerization of n-Butane in the Presence of Aluminum Chloride and Water

Experiment No.	1	2	3	4
Duration of reaction, hrs.	12	12	12	12
Temp., °C.	100	100	100	100
Charge, moles per 100 moles <i>n</i> -Butane				
Aluminum chloride	9.0	9.0	9.0	9.0
Water	9.0	27.4	36.5	54.2
Moles H ₂ O/mole AlCl ₃	1	3	4	6
HCl generated, moles/mole AlCl ₃	0.51	0.46	0.22	0.12
Analysis of hydrocarbons, mole %				
Isobutane	35.1	16.8	11.3	0
<i>n</i> -Butane	63.6	81.9	87.8	100
Pentanes and higher	1.3	1.3	0.9	0

3. Equilibrium Study of Butanes

a. Calculation of Equilibrium Concentrations. The isomerization of butanes and higher paraffin hydrocarbons is a reversible reaction. The equilibrium of isomerization of the butanes, pentanes, hexanes, and heptanes was calculated from the heat of isomerization at 0°K., ΔH_0° , for the normal paraffin to the branched-chain isomer and from the values of the free energy function $(F^\circ - H_0^\circ)/T$, for each isomer (Rossini, Prosen, and Pitzer, 12). For the isomerization of the normal paraffin to the isoparaffin



ΔF° is the standard free energy change at a given temperature, with each component in its ideal standard state of unit fugacity, and

$$\Delta \left(\frac{F^\circ - H_0^\circ}{T} \right) = \left(\frac{F^\circ - H_0^\circ}{T} \right)_i - \left(\frac{F^\circ - H_0^\circ}{T} \right)_n \quad (2)$$

But

$$\Delta \left(\frac{F^\circ - H_0^\circ}{T} \right) = \frac{\Delta F^\circ}{T} - \frac{\Delta H_0^\circ}{T} \quad (3)$$

and

$$\frac{\Delta F^\circ}{T} = -R \ln K \quad (4)$$

where K is the equilibrium constant. Then

$$\frac{\Delta F^\circ}{T} = -R \ln K = \frac{\Delta H_0^\circ}{T} + \Delta \left(\frac{F^\circ - H_0^\circ}{T} \right) \quad (5)$$

For the isomerization reaction as given by eq. 1

$$K = f_i/f_n$$

and, for low pressures

$$K = p_i/p_n$$

where f represents the fugacity and p the partial pressure.

The calculated equilibrium concentration of normal and isobutane is given in Fig. 1; the amount of the two isomers, in mole fractions, is plotted as a function of the temperature.

b. Experimental Determination of Equilibrium Constant. The equilibrium constants for normal and isobutane were established by studying the isomerization of butanes from both the normal and isoparaffin side (Pines, Kvetinskas, Kassel, and Ipatieff, 13). The isomerization was studied at 25, 100, and 150° and under experimental conditions designed to reduce to a minimum the amount of secondary reactions. Depending upon the temperature level investigated, the experiments were carried out in sealed tubes, a stirring autoclave, or a continuous flow type apparatus.

From the experimental results obtained, the concentration of isobutane in liquid and in vapor phase was calculated as a function of temperature. The results summarized in Table XIII are in good agreement with equilibrium determination of other investigators (Moldavskii and Nizovkina, 14), (Montgomery, McAteer, and Franke, 3), (Horne, 15).

TABLE XIII
Isomerization of Butane

Temp. °C.	K_G°/K_L	p_I/p_N	Mole % Isobutane	
			liquid	vapor
20	1.410	1.439	81.7	86.3
25	1.395	1.426	80.9	85.5
30	1.378	1.412	80.0	84.7
40	1.348	1.389	78.4	83.0
50	1.319	1.368	76.8	81.3
60	1.290	1.350	75.2	79.6
70	1.264	1.334	73.6	77.9
80	1.238	1.319	72.1	76.2
90	1.215	1.306	70.7	74.5
100	1.193	1.294	69.2	72.9
110	1.175	1.282	67.8	71.2
120	69.6
130	68.0
140	66.5
150	65.0

All the values agree within a maximum deviation of 3% in composition

with values based on the equation

$$R \ln K_G^\circ = (2318/T) - 4.250,$$

where K_G° is the vapor phase equilibrium constant at zero pressure, and T is temperature expressed in $^\circ\text{K}$.

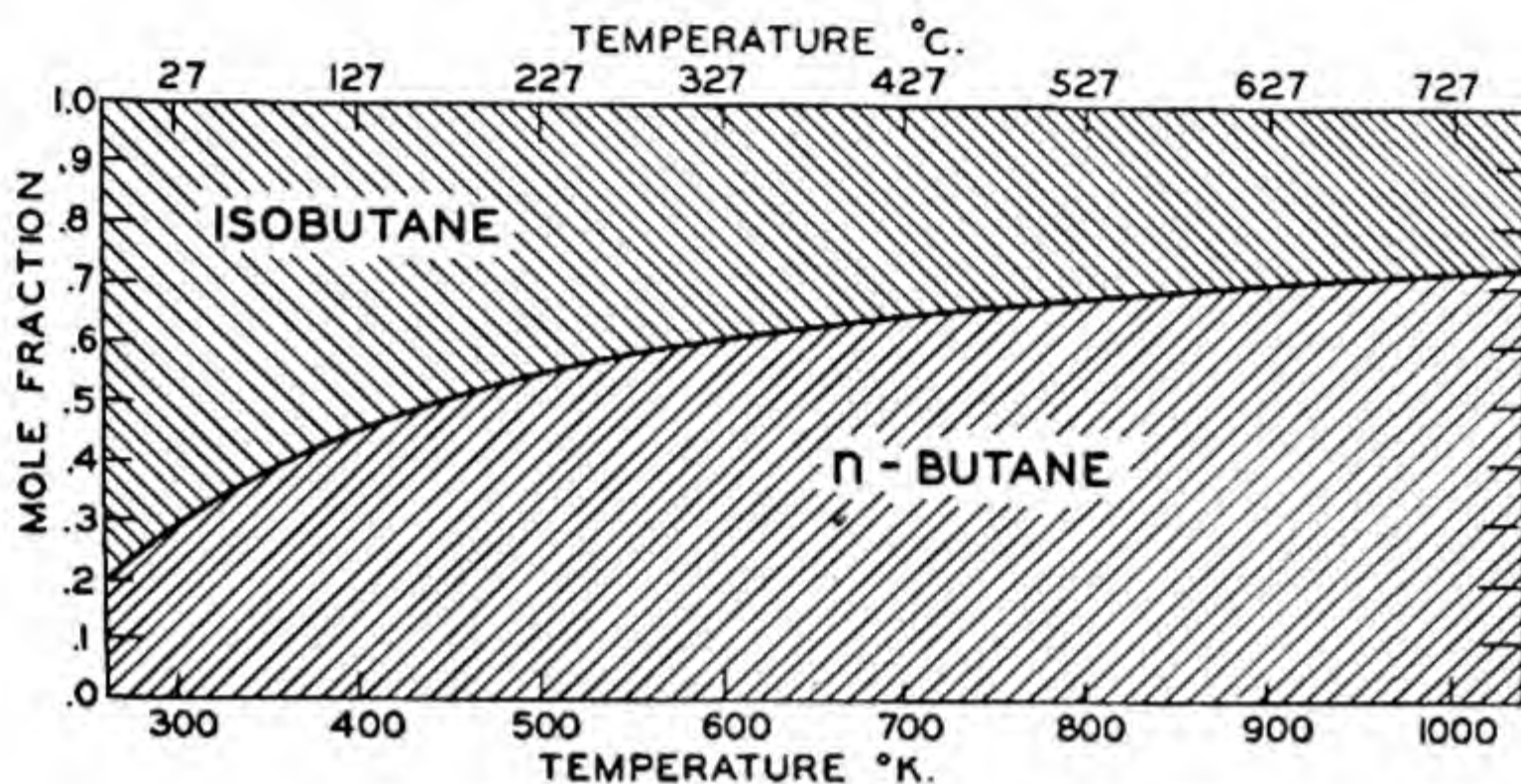


FIG. 1. Equilibrium concentrations of the butanes.

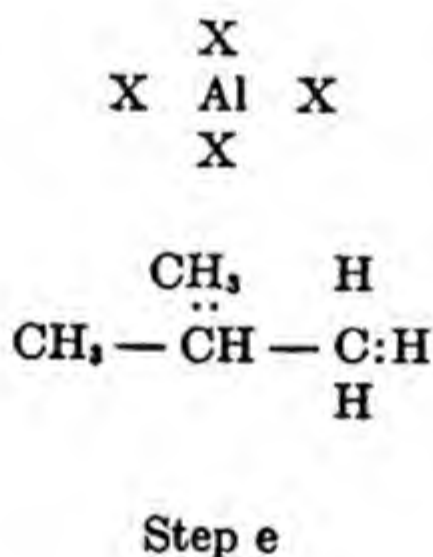
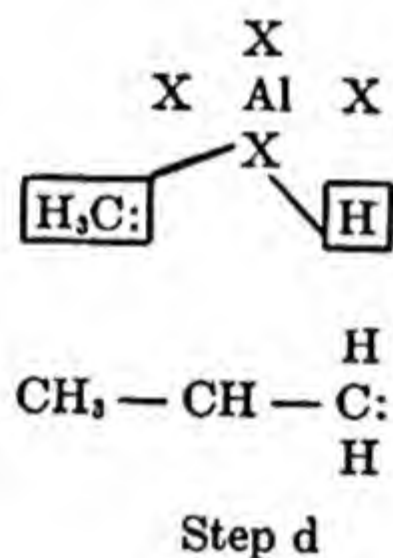
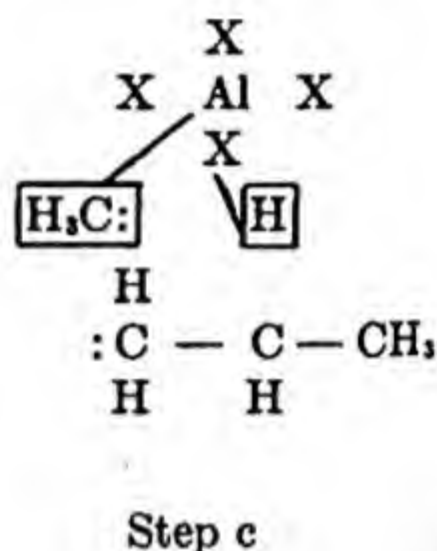
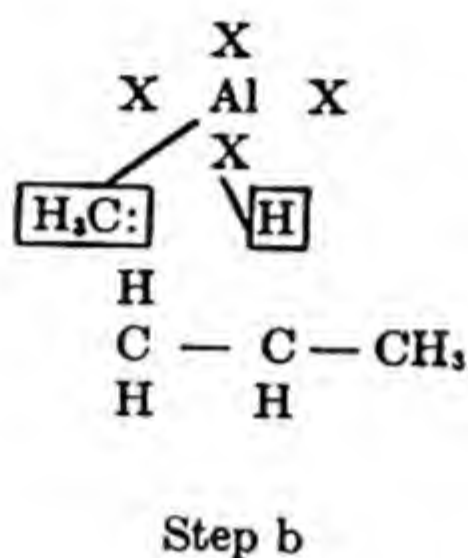
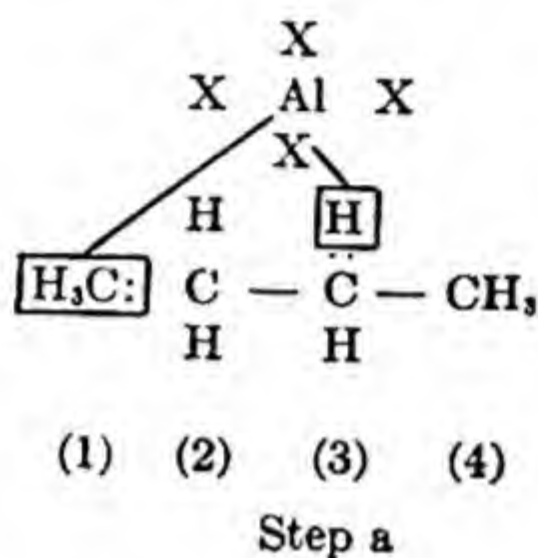
4. Mechanism of Isomerization

Various mechanisms have been suggested to explain the isomerization of butanes.

a. Heldman Mechanism. This mechanism (Heldman, 16) is based primarily on the observation that (a) dry, pure aluminum bromide and aluminum chloride are not isomerization catalysts unless a hydrogen halide or substance capable of producing the same type of reaction with aluminum halide (e.g., water, alkyl halides, sodium halides, etc.) is present; (b) under mild conditions, isomerization is the only reaction observed with butanes. With the higher molecular weight paraffins, and with all paraffins at higher temperatures, simultaneous disproportionation and "cracking" may also proceed.

Heldman assumed that aluminum exhibits a coordination number greater than 4 during isomerization and considered AlX_4^- a catalyst, which acts as both an acid and a base. He suggested that: (a) at first there is an oriented collision of the catalyst with the paraffin. This produces a configuration in which a hydrogen from the carbon atom $[\text{C}_{(3)}]$ in the butane chain is near a halogen of the catalyst and the methyl group $[\text{C}_{(1)}]$ is near the aluminum (Step 1, see below). (b) AlX_4^- acts as an acid toward the end methyl group and as a base toward the hydrogen. In this manner a transient activated complex is formed with the methyl and hydrogen loosely attached to the catalyst. The hydrocarbon residue is restrained

from moving from the vicinity by the residual attraction of the :CH_3 and H. (c) A shift then occurs of an electron pair from the middle to the new end carbon of the hydrocarbon fragment. (d) Concomitantly, the fragments rotate with respect to the catalyst, so that the latter is brought into a new position with the :CH_3 and H adjacent to the middle and end carbon atoms respectively. (e) Reattachment yields isobutane as the product. According to Heldman's mechanism, the isomerization of *n*-butane proceeds as follows:

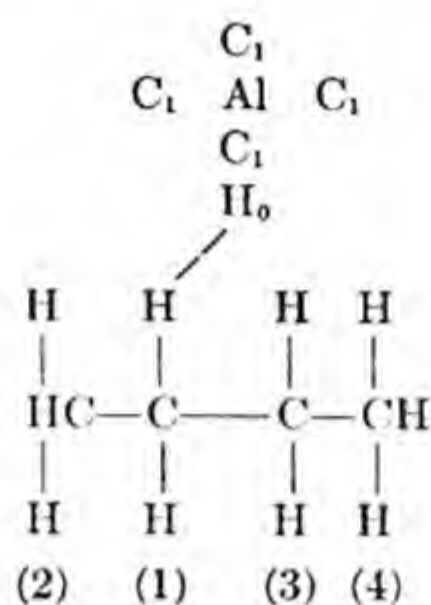


b. Powell and Reid Mechanism. Tritium, the radioactive hydrogen isotope, H^3 , was utilized to determine the steps involved in the reversible isomerization of *n*-butane to isobutane (Powell and Reid, 17). The catalyst used for this study consisted of aluminum chloride supported on alumina or charcoal. The isomerization experiments were carried out at atmospheric pressure with temperatures in the range of 107–128°. The experiments consisted in passing the following mixture of gases over the catalysts: (a) tritium hydride and butanes; (b) tritium hydride, hydrogen chloride, and butanes; (c) tritium butyl and hydrogen.

It was found that exchange between hydrogen and tritium always took place, and that both *n*- and isobutane contained tritium. The degree of exchange was proportional to the degree of isomerization. The great extent of exchange with hydrogen chloride was attributed to its integral participation in the reaction where the exchange of hydrogen atoms between butanes

and molecular hydrogen is owing to the vulnerability to attack by hydrogen of the butane molecule in the process of isomerization.

The following steps were proposed for the isomerization of *n*-butane to isobutane: "1. The butane contacts the catalyst mass in such a manner that the hydrogen of the hydrogen chloride in combination with aluminum chloride (designated as H_0 in the diagram) enters the bonding sphere of the carbon atoms (designated as C_1) of the butane.



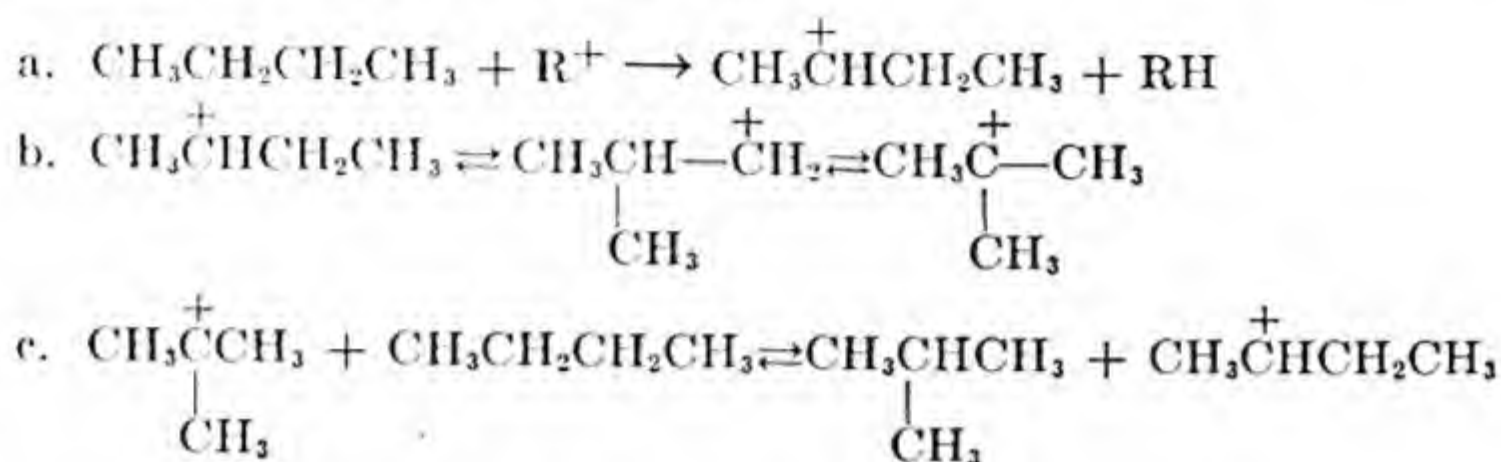
2. A weakening of the bond between C_1 and C_2 with a partial rupture occurs because of the presence of three hydrogen atoms and two carbon atoms about the same bonding volume of C_1 . 3. At this point, the $AlCl_3$ exists essentially minus its hydrogen in a position intermediate between C_1 and C_3 . In such a position, there is a tendency to acquire a hydrogen from C_3 thus leaving a situation of unfilled bond position distributed between C_1 and C_3 so that the methyl group C_2 may either become bonded with C_3 to form isobutane or reattach itself to C_1 to return to the original normal butane form."

According to the authors, the exchange of tritium from hydrogen to butane probably takes place at the point represented at the beginning of step 3. The reverse reaction, isobutane to *n*-butane is explained by the same steps in reverse order.

The formation of hydrogen aluminum tetrachloride, as assumed in step 1, does not seem plausible in view of the reported recent work (Brown and Pearsall, 18) which indicated that this compound is nonexistent. The interaction of aluminum chloride and hydrogen chloride does presumably occur in the presence of olefins.

c. Chain Mechanism. (1) Effect of olefins. The mechanism described above (Section II, 4a and 4b) did not take into consideration the fact that under controlled conditions *n*-butane does not undergo isomerization in the presence of aluminum halide-hydrogen halide catalyst unless traces of olefins or their equivalent are present (Pines and Wackher, 7). In order to explain the role of olefins in isomerization, a chain mechanism was proposed

(Bloch, Pines, and Schmerling, 19). This mechanism postulated that the isomerization of *n*-butane proceeds in the presence of aluminum halide and hydrogen halide by a sequence of reactions which may be expressed as follows in terms of carbonium ions.



Reaction a serves only to initiate the chain and the reactant, R^+ , need therefore be present in small amount only. The chain initiating ion, R^+ , may be produced in several ways. It may be formed in the presence of aluminum halide by the addition of hydrogen halide to an olefin which is present in the paraffin as an impurity, or which is added as such, or results from the cracking of the paraffin. It may also be introduced in the form of an alkyl halide. The rearrangement of the *s*-butylcarbonium ion (b) finds analogy in the rearrangement of olefins in the presence of acidic substances (Whitmore, 20; Egloff, Hulla, and Komarewsky, 21). The reaction of a and c is similar to the hydrogen-halogen exchange reaction which occurs when isoparaffins are contacted with *s*- or *t*-alkyl halides in the presence of aluminum halide (Bartlett, Condon, and Schneider, 22).

TABLE XIV

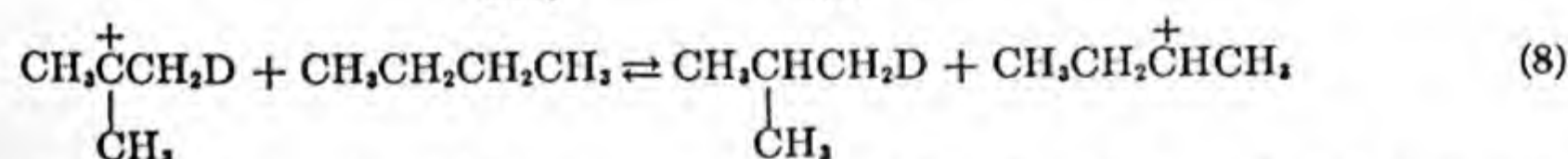
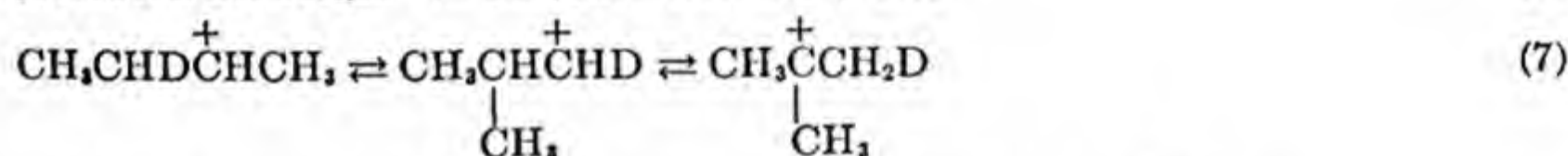
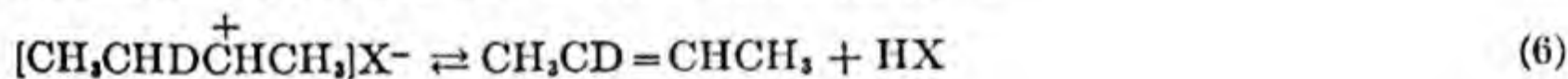
*Isomerization of n-Butane in the Presence of
Aluminum Bromide-Deuterium Bromide Catalyst*

Experiment No.	1	2	3	4
Reaction time, hrs.	20	20	20	7
Temp., °C.	25	25	25	25
Charge, mole				
AlBr ₃	0.01151	0.01021	0.01171	0.01031
DBr	.01054	.00942	0.1170	.01045
<i>n</i> -Butane	.1239	0	.1173	.1060
Isobutane	0	0.1156	0	0
Butenes	0	0	116×10^{-6}	98×10^{-6}
Analyses of reaction product, moles %				
DBr + HBr	7.9	6.3	9.4	8.1
Isobutane	0.0	93.3	36.6	19.1
<i>n</i> -Butane	92.1	0.4	53.0	72.4
Pentanes and higher	0.0		1.0	0.4
Per cent originally present as DBr found in butanes	6.0	9.5	92.0	84.8

In order to test the validity of the postulated mechanism of isomerization, deuterium bromide-aluminum bromide instead of hydrogen bromide-aluminum bromide was used as an isomerization catalyst (Pines and Wackher, 23). The reactions were carried out under controlled conditions using a high-vacuum technique. The experimental conditions are summarized in Table XIV.

It was found that by treating either *n*-butane or isobutane with 10 mole % deuterium bromide-aluminum bromide catalyst for 20 hours at 25°, no isomerization of the butanes occurred and only 6 and 9.5% of the deuterium exchanged with *n*-butane and isobutane, respectively. When, however, 0.1 mole % butenes was added to *n*-butane and the isomerization reaction was carried out under the same experimental conditions, over 40% of the butane isomerized to isobutane and 92% of the deuterium underwent an exchange reaction. These results indicate clearly that olefins take an active part in isomerization. The results obtained are in agreement with the proposed mechanism of isomerization.

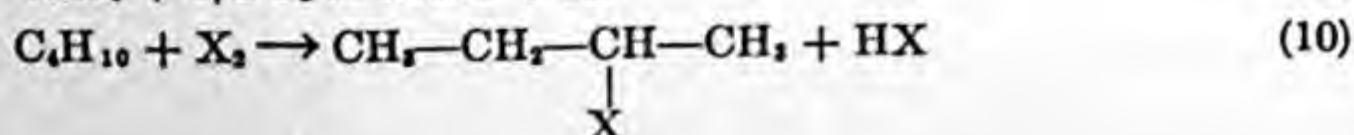
The exchange reaction occurring in the presence of aluminum bromide between deuterium of the deuterium bromide and hydrogen of butanes, when small amounts of olefins are present, can be represented by the equations:



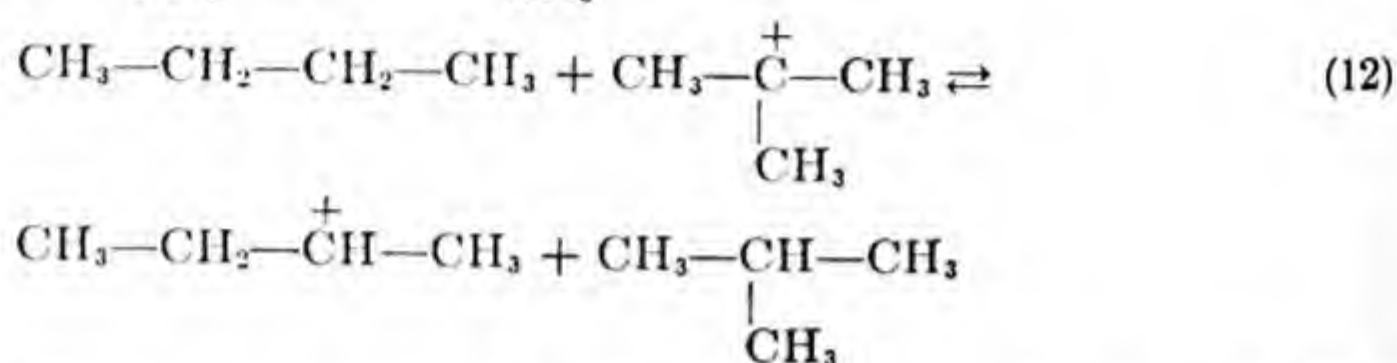
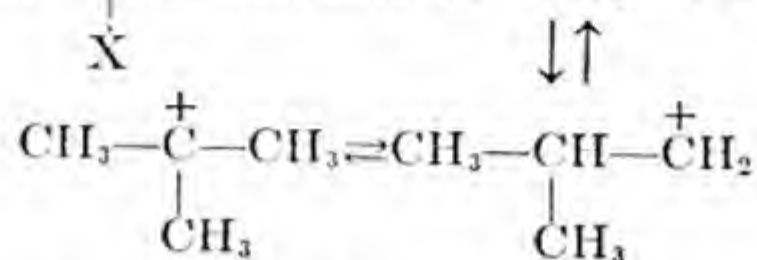
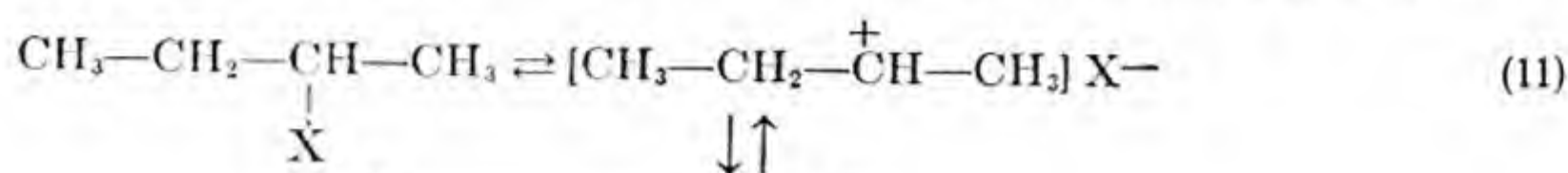
The deuterization of *n*-butane can also take place by applying the same reasoning as given above. The equations also show the possibility of the existence of more than one atom of deuterium in a molecule of butane.

(2) Effect of oxygen. Two hypotheses were proposed to explain the effect of oxygen upon the isomerization of *n*-butane in the presence of either aluminum chloride or aluminum bromide (Pines and Wackher, 8). Both hypotheses assume the formation of hydrogen halide and alkyl halide; the latter acting as a chain starter for isomerization.

Hypothesis A. Aluminum halide reacts with oxygen to yield aluminum oxyhalide and halogen. The latter reacts with the alkanes to form alkyl halides and hydrogen halide.



The reaction represented in eq. (10) proceeds much faster in the presence of sunlight; the consumption of halogen causes a shift of the equilibrium toward the right in eq. (9). The alkyl halide formed (eq. 10) acts, in the presence of catalysts, as a chain starter for the isomerization of alkanes.



Hypothesis B. Alkanes are oxidized in the presence of aluminum halide to form

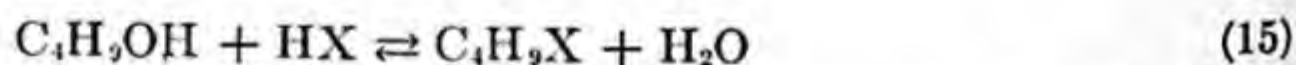


The use of aluminum chloride as an oxidation catalyst was described in the literature (Friedel and Crafts, 24).

The butanol formed (eq. 13) may react with aluminum halide to form butoxyaluminum dihalide (Tsukervanik and Tokareva, 25).



Part of the butanol may also react with the hydrogen halide formed, according to the following equation:



The alkyl halide produced may act then as a chain starter for the isomerization of butane as given in eq. (11) and (12).

In order to throw some light upon the validity of hypothesis A, the effect of oxygen upon aluminum bromide was investigated. It was found that by treating aluminum bromide with pure oxygen at room temperature, a slight but definite reaction occurred, as evidenced by coloration caused by liberated bromine. The product of such oxidation, after the removal of unreacted oxygen, showed slight catalytic properties toward the isomerization of *n*-butane, yielding 6.6–13.8% isobutane. The treatment of aluminum bromide at 100° with an approximately equal molal mixture of oxygen and nitrogen did not seem to increase the degree of oxidation. The experimental results are given in Table XV. The fact that the oxidation of aluminum bromide by pure oxygen or oxygen-nitrogen mixture is slow does

not exclude the possibility that in hydrocarbon solution it may proceed much faster, especially since the liberated bromine reacts with hydrocarbons and therefore is removed from the reaction zone.

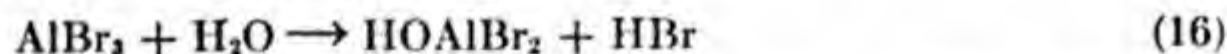
TABLE XV

*Effect of Pretreatment of Aluminum Bromide
with Oxygen upon the Isomerization of n-Butane*

Experiment No.	1	2	3	4
Reaction time, hrs.	138	117	141	119
Temp., °C.	25	25	25	25
Charged:				
Aluminum bromide, g.	3.04 ^a	3.18 ^b	2.24 ^c	2.28 ^d
n-Butane, g.	7.07	7.45	5.20	6.34
AlBr ₃ moles/100 moles butane	9.32	...	9.36	7.38
Hydrocarbons recovered, g.	6.90	7.22	5.25	6.23
Analyses, mole %				
Isobutane	9.2	6.2	6.6	13.8
n-Butane	89.5	93.5	92.3	86.0
Pentanes and higher	1.3	0.3	1.1	0.2

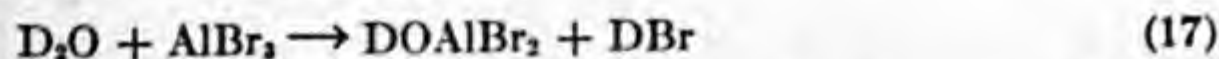
^a The aluminum bromide was treated with 170 cc. (at s.t.p.) oxygen at 20–25° for 476 hours, after which the reaction vessel was kept in liquid nitrogen and the oxygen was pumped off to 10⁻² mm. mercury pressure. ^b Treated with 170 cc. oxygen at 20–25° for 693 hours; the reaction vessel was kept at 0° while being pumped out. ^c The aluminum bromide was treated with 150 cc. oxygen-nitrogen mixture (46.3% O₂ and 53.7% N₂) at 100° for 1 hour. The vessel had a reddish tint because of the liberated bromine. The gases were pumped out at room temperature; 140 cc. gas was recovered. ^d Treated with 135 cc. nitrogen-oxygen mixture (48.2% O₂ and 51.8% N₂) at 100° for 13 hours; 120 cc. gas consisting of 46.9% O₂ and 53.1% N₂ was pumped out at room temperature and at 10⁻² mm. pressure. From the analysis obtained it was calculated that only 9 mole % aluminum bromide underwent oxidation to form assumedly AlOBr.

(3) Effect of water. It was found (Section II, 2d) that by contacting 1 mole equivalent of water with 1 mole equivalent aluminum bromide (AlBr₃), 1 mole equivalent hydrogen bromide is liberated, while all of the aluminum bromide reacted (Wackher and Pines, 11). The reaction proceeded probably according to eq. (16).



It was shown that hydroxyaluminum dibromide is an effective catalyst for the isomerization of n-butane even in the absence of hydrogen bromide and/or added olefins.

In order to determine whether the halogen or the hydrogen of the hydroxyaluminum dibromide was the active part of the catalyst, deuterioxyaluminum dibromide was prepared by the action of deuterium oxide on aluminum bromide (Pines and Wackher, 23).



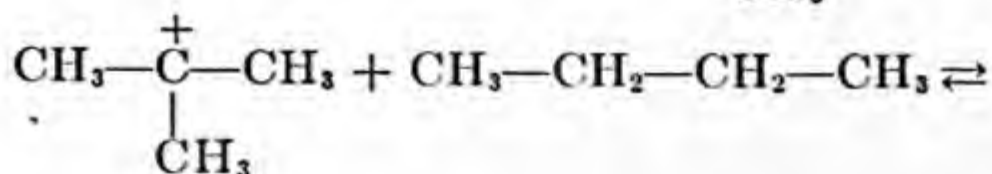
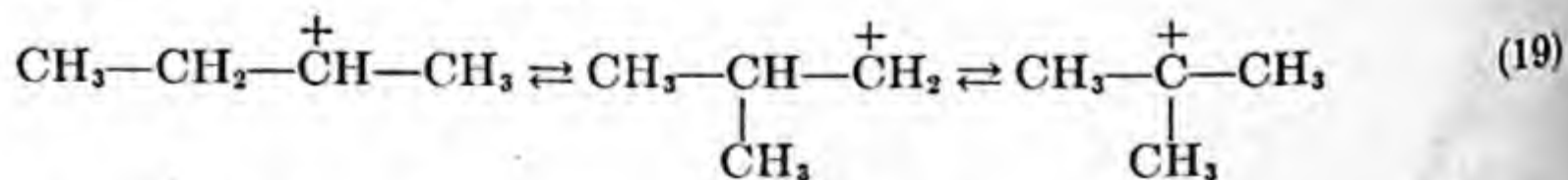
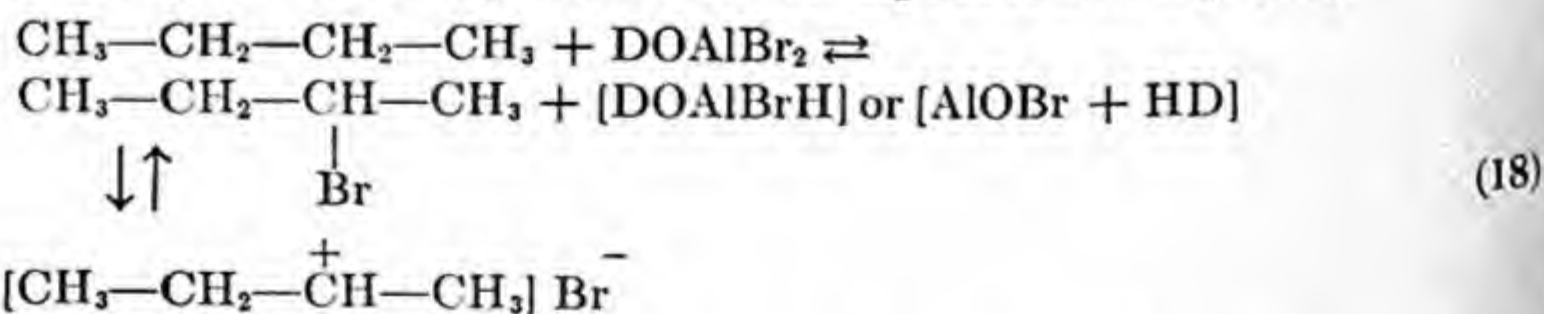
It was found that by carrying out the isomerization in the presence of the deuterioxyaluminum dibromide and under essentially the same experimental

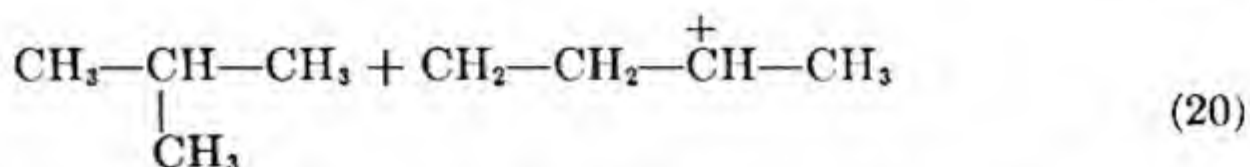
conditions as for experiment 1, Table IX, 5.4% of deuterium underwent an exchange reaction although 21% isomerization of *n*-butane to isobutane occurred. The degree of hydrogen-deuterium exchange reaction is not proportional to isomerization; virtually the same percentage of exchange was noticed in a reaction in which the degree of isomerization of *n*-butane to isobutane was only 3.7%.

TABLE XVI
*Reaction of Aluminum Bromide with Deuterium Oxide
and Isomerization of n-Butane in the Presence of the Resulting Reaction Product*

A			
Experiment No.		1	2
Reaction time, hrs.:	at 25°	16	17
	at 100°	0.5	0.75
Charge:			
Aluminum bromide, moles		0.01175	0.01137
Deuterium oxide, moles		0.01177	0.01142
Moles D ₂ O per mole AlBr ₃		1.00	1.00
Deuterium bromide generated			
Moles per mole AlBr ₃		1.00	1.04
B			
Isomerization of <i>n</i> -butane in the presence of the catalyst described in A. Isomerization of <i>n</i> -butane in the presence of DOAlBr ₂ .			
Reaction time, hrs.		20	42
Reaction temp., °C.		25.0	25.0
<i>n</i> -Butane charged, moles		0.1189	0.1179
Analysis of product, mole % HBr and DBr		0.0	0.6
Isobutane		3.7	21.0
<i>n</i> -Butane		96.3	78.1
Pentanes and higher		0.0	0.3

From the above it was concluded that the isomerization of *n*-butane by means of hydroxyaluminum dibromide involves the bromine atoms. The isomerization proceeds probably through a chain reaction. The chain is probably initiated by an exchange reaction as expressed in eq. (18).





The steps expressed in eq. (19) and (20) are the same as described in section II, 4c (1).

Recent experiments (Beeck *et al.*, 25a) on the isomerization of propane-1-C¹³ to propane-2-C¹³ further demonstrate that the isomerization proceeds through an intramolecular rearrangement. No propane containing more than one C¹³ carbon atom per molecule was found. These experiments were made by contacting vapors of propane at approximately 25° and 450 mm. pressure with a catalyst prepared by the addition of 0.023 g. water to 0.40 g. anhydrous aluminum bromide for periods of time varying from 0 to 1074 hours. It was found that the rate of isomerization of propane-1-C¹³ to propane-2-C¹³ is comparable to the rate of isomerization of *n*-butane to isobutane under similar conditions. The equilibrium distribution of the propanes-1-C¹³ and -2-C¹³ was found to be statistical, that is, propane-1-C¹³/propane-2-C¹³ = 2.

The mechanism by which propane isomerizes can also be explained by means of a chain mechanism, in a similar way as was done for butanes.

5. Commercial Methods for the Isomerization of *n*-Butane

During World War II, the great demand for aircraft fuel necessitated the production of large quantities of isobutane, a basic raw material in the production of high octane aviation gasoline. (See chapter on Alkylation of Alkanes.*) Various processes have been developed for the isomerization of *n*-butane to isobutane; all of them employed aluminum chloride-hydrogen chloride as catalyst. The difference between the various processes consisted either in the method of introduction of aluminum chloride to the reaction zone, the catalyst support, or the state of the catalyst. The following summary describes some of the main features of the various processes which were developed:

a. The isomerization is carried out by mixing *n*-butane with a controlled quantity of hydrogen chloride and passing it at a temperature of 95–150° and under a pressure of 9–18 atmospheres over a catalyst composed of aluminum chloride supported on a granular alumina carrier (Cheney and Raymond, 26). The effluent from the reactor, after being cooled and condensed, enters an accumulator. Liquid from this accumulator is pumped to the hydrogen chloride stripping column where hydrogen chloride was removed as the top product and is recycled to the feed stream. Isobutane is separated then from *n*-butane and the latter repassed through the catalyst. The average conversion of *n*-butane to isobutane was 45%.

b. This process consists in a continuous addition of aluminum chloride into the reaction zone, thereby maintaining the activity of the catalyst constant (Chenicek *et al.*,

* See Ipatieff and Schmerling, *Advances in Catalysis*, vol. II, in preparation.

27). This process has been developed by taking advantage of the fact that aluminum chloride is slightly soluble in liquid *n*-butane. Thus a definite amount of aluminum chloride is continuously introduced into the reactor at constant rate by first passing all or a portion of the *n*-butane charge, in the absence of hydrogen chloride, through a heated zone called the saturator which contains granular aluminum chloride. The quantity of aluminum chloride so introduced is accurately controlled by the temperature at which the saturator is maintained and by the volume of butane passing through.

The reactor in which the isomerization occurs is packed with quartz chips. The hydrocarbon stream from the saturator, containing aluminum chloride, enters the top section of the reactor and is mixed with another hydrocarbon stream containing the hydrogen chloride. The hydrocarbon effluent from the reaction zone which also contains hydrogen chloride and dissolved aluminum chloride, enters recovery sections. An aluminum chloride-rich stream is separated by distillation and recycled to the unit. Subsequently hydrogen chloride is separated and recycled. Isobutane produced is separated from *n*-butane by fractional distillation. The isomerization is carried out at a temperature range of 50–120°, with the maximum conversion and greatest catalyst life at the lower end of the range. The isobutane content of the product is up to 50%.

c. The catalyst used in this process consists of anhydrous aluminum chloride dissolved in antimony trichloride together with hydrogen chloride (McAllister, Ross, Randlett, and Carlson, 28). The isomerization is carried out in a continuous manner employing continuous rejection of spent aluminum chloride and continuous catalyst make-up so that the catalyst is maintained at a constant high level of activity. The conditions used for liquid phase butane isomerization are: aluminum chloride content of the catalyst 9–10%, hydrogen chloride content of feed 5% by weight, temperature of isomerization 80–90°, and a pressure of 20 atmospheres. Average contact time of the reaction is 12 minutes. The conversion per pass of normal to isobutane amounts to 54%.

d. The main feature of this process is to use a solid catalyst composed of aluminum chloride-bauxite and to maintain the activity of the catalyst by the introduction of fresh aluminum chloride with the feed (Perry, 38).

The dried butene is vaporized and superheated to the desired temperature and passed on the reactor which contains substantially dehydrated, low iron-content bauxite (Porocel). A controlled portion of the superheated vapor is passed through a vessel charged with aluminum chloride prior to entering the reactor. Aluminum chloride thus is vaporized and fed into the reactor as required and is adsorbed on the bauxite. This technique enables the catalyst to be maintained in a relatively uniform and high state of activity.

Typical reaction conditions and results are as follows: temperature, 120–150° C.; pressure, 14–17 atmospheres; feed rate, 0.5–1.0 volumes liquid butane per volume of bauxite per hour; conversion to isobutane, 40–50%; catalyst life, 180 gallons isobutane per pound of aluminum chloride, or 60 gallons isobutane per pound of bauxite.

III. ISOMERIZATION OF PENTANES

1. *Without cracking suppressors*

In the first systematic study of the isomerization of *n*-pentane it was found that freshly sublimed aluminum chloride does not catalyze the isomerization of *n*-pentane even on refluxing for several days (Glasebrook, Phillips, and Lovell, 29). When, however, a small amount of water, alkyl

halide, or hydrated aluminum chloride was added to the reaction mixture, the *n*-pentane commenced to undergo reaction almost immediately; butanes and isopentane could be identified, the latter being the chief product. Substances boiling above *n*-pentane were also formed, but owing to the small amount present, could not be characterized. During the reaction the catalyst became coated with a layer of brown tar, which, after the hydrolysis, yielded a mixture of highly unsaturated, halogen-containing compounds.

When gaseous *n*-pentane carried by a stream of nitrogen was passed over aluminum chloride at a temperature from 40 to 133°, no reaction could be detected outside of a small discoloration of the aluminum chloride. The addition of hydrogen chloride caused the decomposition of *n*-pentane even at 40°.

Aluminum bromide proved a much more effective catalyst in causing the decomposition of *n*-pentane, and it was unnecessary knowingly to add other substances to the reaction mixture to induce reaction. It was found that *n*-pentane containing 1.5 mole % aluminum bromide underwent as much change as *n*-pentane containing 17.4 mole % aluminum chloride. The butanes formed increased practically linearly with the extent of the reaction, whereas the isopentane reached a maximum from which it slowly declined as the extent of the reaction was further increased.

The effect of aluminum bromide concentration, reaction time, and promoters is given in Tables XVII, XVIII, and XIX.

2. Cracking suppressors

It has been shown that the isomerization of *n*-pentane in the presence of aluminum chloride or aluminum bromide containing catalysts was accompanied by side reactions, characterized by the formation of butanes and tarry material. These side reactions can be inhibited by the use of hydrogen or organic additives.

TABLE XVII

The Effect of Aluminum Bromide Concentration on the Decomposition of n-Pentane

Experiment No.	1	2	3	4
<i>n</i> -Pentane used, g.	110	110	110	110
Aluminum bromide, mole %	1.5	5.3	8.9	14.1
Reaction loss, wt. %	1.5	0.9	3.2	6.8
Products obtained:				
Butanes, volume %	1.5	6.1	10.2	14.1
Isopentane, volume %	27.2	53.5	46.8	40.4
Material boiling higher than <i>n</i> -Pentane, volume %	2.8	3.1	5.4	5.9

The duration of the reaction was 26.2 hours.

TABLE XVIII

The Effect of Reaction Time on the Decomposition of n-Pentane

Experiment No.	1	2	3	4
Reaction time, hrs.	22	51	95	169
Products obtained:				
Butanes, volumes %	1.5	2.8	5.0	8.8
Isopentane, volume %	40.8	51.0	55.9	44.2
Material boiling higher than <i>n</i> -pentane, volume %	2.5	3.4	3.4	5.9

One hundred and five grams of *n*-pentane was used in each experiment; the concentration of aluminum bromide was 2.8 mole %.

TABLE XIX

The Effect of Promoters in the Reaction of n-Pentane in the Presence of Aluminum Bromide

Experiment No.	1	2	3	4
	With 2 ml. of water added	Without water	In the presence of hydrogen bromide	In the absence of hydrogen bromide
<i>n</i> -Pentane used, g.	200	200	202	202
Aluminum bromide, mole %	3.5	3.8	2.4	2.4
Reaction time	About 3 days		About 38 hrs.	
Reaction loss and tar, wt. %	3.0	1.5	2.5	negative
Products obtained:				
Butanes, volume %	10.7	5.0	7.0	3.0
Isopentane, volume %	58.6	51.0	51.5	42.8
Material boiling higher than <i>n</i> -pentane, volume %	6.0	2.7	2.5	3.6

(a) *Effect of Hydrogen.* The use of hydrogen under pressure as a method for inhibiting side reaction during the isomerization of *n*-pentane has been reported by various investigators (Schuit, Hoog, and Verheus, 4), (Ipatieff and Schmerling, 30), (Evering *et al.*, 31).

A systematic study of the isomerization of *n*-pentane was carried out in a rotating autoclave of 850 ml. capacity (30). The catalyst and *n*-pentane were weighed into a glass liner equipped with a ground glass capillary stopper. The open autoclave was flushed with nitrogen and the liner was sealed into it. Most of the gas was then removed by applying suction for 2 minutes. Finally, a weighed amount of hydrogen chloride (if used) was pressed in and the pressure was raised to 100 atmospheres with hydrogen or nitrogen. The autoclave was then heated to the desired temperature for 4 hours, after which it was permitted to set overnight.

The experimental results obtained, summarized in Table XX, show that

TABLE XX
Effect of Hydrogen upon the Isomerization of *n*-Pentane

Experiment No.	1	2	3	4	5	6	7	8	9	10
Aluminum chloride										
Gas	N ₂	H ₂	H ₂	H ₂	H ₂	N ₂ ^a	H ₂ ^a	H ₂	H ₂	H ₂
Temp., °C.	125	125	125	125	125	125	125	100	125	150
Reactants, g.										
<i>n</i> -Pentane	100	100	100	100	100	100	100	100	363	100
Aluminum chloride	10	10	10	10	12	10	10	10	35	10
Hydrogen chloride	0	0	2	10	1.6	0	0	0	0	0
Recovered catalyst, g.	16	10	10	10	12	15	13	10	37	10
Composition of product, mole %										
Methane, ethane, propane	12.9	0	0	0	4.0	4.6	4.2	0	5.8	20.8
Isobutane	27.6	0	0	0.5	1.4	47.4	0	3.2	0	1.4
<i>n</i> -Butane	18.4	0	0	0	0	2.8	0		0.1	2.5
Isopentane	5.5	2.8	22.4	61.0	73.7	30.6	93.4	14.2	84.9	65.2
<i>n</i> -Pentane	25.4	96.6	77.3	38.0	18.8	3.3	2.4	82.6	9.2	10.1
Hexanes and higher	10.2	0.6	0.3	0.5	2.1	11.3	0	0	0	0

^a The initial pressure was 25 atmospheres, in all the other experiments the initial pressure was 100 atmospheres.

little reaction occurred when *n*-pentane was heated with aluminum chloride and hydrogen at 125°. When the reaction was carried out under nitrogen pressure, side reactions occurred; butanes, hexanes, and higher boiling alkanes were formed and the catalyst was converted to a viscous red liquid.

Isomerization did take place under hydrogen pressure when hydrogen chloride was used as a promoter. The yield of isopentane increased with the amount of hydrogen chloride used.

A yield of 74% isopentane was obtained when a small amount of water instead of hydrogen chloride was added to the reagents.

The purity of aluminum chloride plays an important role in the activity of the catalyst. Technical aluminum chloride, containing 15 to 20% unsublimable product, was an excellent catalyst even in the absence of added hydrogen chloride; 85% of the *n*-pentane was converted to isopentane. On the other hand, isomerization of about one-third and auto-destructive alkylation of almost all of the remaining two-thirds of the pentane charge occurred when nitrogen was substituted for hydrogen.

The temperature of the reaction affects the degree of isomerization and decomposition; at 100°, 14% and at 125°, 85% of the *n*-pentane isomerized to isopentane; at 150°, however, 25% of the material recovered consisted of gaseous alkanes.

The effect of various hydrogen pressures upon the inhibition of the disproportionation of pentanes was investigated (Evering *et al.*, 31). The reaction was carried out in a 1490 ml. capacity reactor which was stirred mechanically. The reactor was jacketed so that it could be quickly heated by steam or cooled by water. Provisions were made for the withdrawal of the liquid product from the settled aluminum chloride catalyst. The experimental results obtained are summarized in Table XXI.

TABLE XXI

Effect of Hydrogen Pressure Upon Isomerization of Pentanes

Experiment No.	1	2	3	4
Hydrogen pressure, atm.	6.7	10.2	13.6	17.0
Products formed:				
Weight % condensibles	69.5	2.3	2.2	1.8
Per cent isopentane (based on pentanes)	71	71	71	64

One liter of pentanes, composed of 12% isopentane and 88% *n*-pentane, 72 g. aluminum chloride, and 20.5 g. hydrogen chloride were used in each experiment. The temperature of the reaction was 100° and the duration 2 hours.

The results show that a minimum effective hydrogen pressure of 8.9 atmospheres exists at 100°. This critical pressure, however, is dependent

both on temperature and on catalyst activity. Increasing hydrogen pressure above this critical value retards isomerization, as well as effecting a slight additional decrease in the disproportionation reaction.

b. Effect of Organic Additives. The effect of organic additives in controlling side reactions in the isomerization of *n*-pentane to isopentane in the presence of aluminum chloride-hydrogen chloride catalysts has been described. The organic additives best suited for decomposition inhibitors are mainly naphthenic and aromatic hydrocarbons and to some extent, isobutane.

Batch and continuous types of experiments were carried out in order to study the effect of additives upon the isomerization of *n*-pentane (Mavity *et al.*, 32). Batch type experiments were carried out in a turbomixer type autoclave. Relatively small amounts of material sufficed in this type of test, which permitted a rather rapid survey of a wide variety of additives.

The continuous tests were directed toward practical application of the method. A sketch of the equipment used for the continuous tests is shown in Fig. 2. The blend of pentane and additive was pumped at a constant rate into the bottom of the saturator from a calibrated pressure charger by means of a high pressure differential plunger pump consisting of a steel tubing 91.5-cm. long and with a 2.5-cm. inside diameter. This was packed at the start of each run with granular, anhydrous aluminum chloride.

The effluent from the saturator, consisting of a solution of aluminum chloride in the charging stock, was discharged to the top of the reactor. The reactor was packed in some instances with 0.6-cm. semiporcelain Berl saddles, in others with 3-8 mesh quartz rock chips.

Effluent from the bottom of the reactor passed into a settling trap from which accumulated sludge, i.e., hydrocarbon-catalyst complex, was periodically discharged. The hydrocarbon-hydrogen chloride stream was released through an automatic pressure control valve and was continuously washed in two glass towers containing water and caustic, respectively. The hydrocarbons were collected in receivers refrigerated by dry ice.

Anhydrous hydrogen chloride was admitted at a definite rate at the top of the reactor.

(1) Aromatic hydrocarbons. Benzene. An outstanding fact in connection with the use of aromatic hydrocarbons as cracking inhibitors is that the concentration required is very low. The criticality of aromatic concentration for the case of benzene is strikingly demonstrated in Fig. 3 and Table XXII. The experiments on which the graph is based were carried out in the continuous type apparatus, at 100°, at a pressure of 7.2-30.4 atmospheres, and using 10 mole % hydrogen chloride on hydrocarbons charged. In Fig. 3 both the degree of isomerization as indicated by the isopentane concentration in the pentane fraction, and the extent

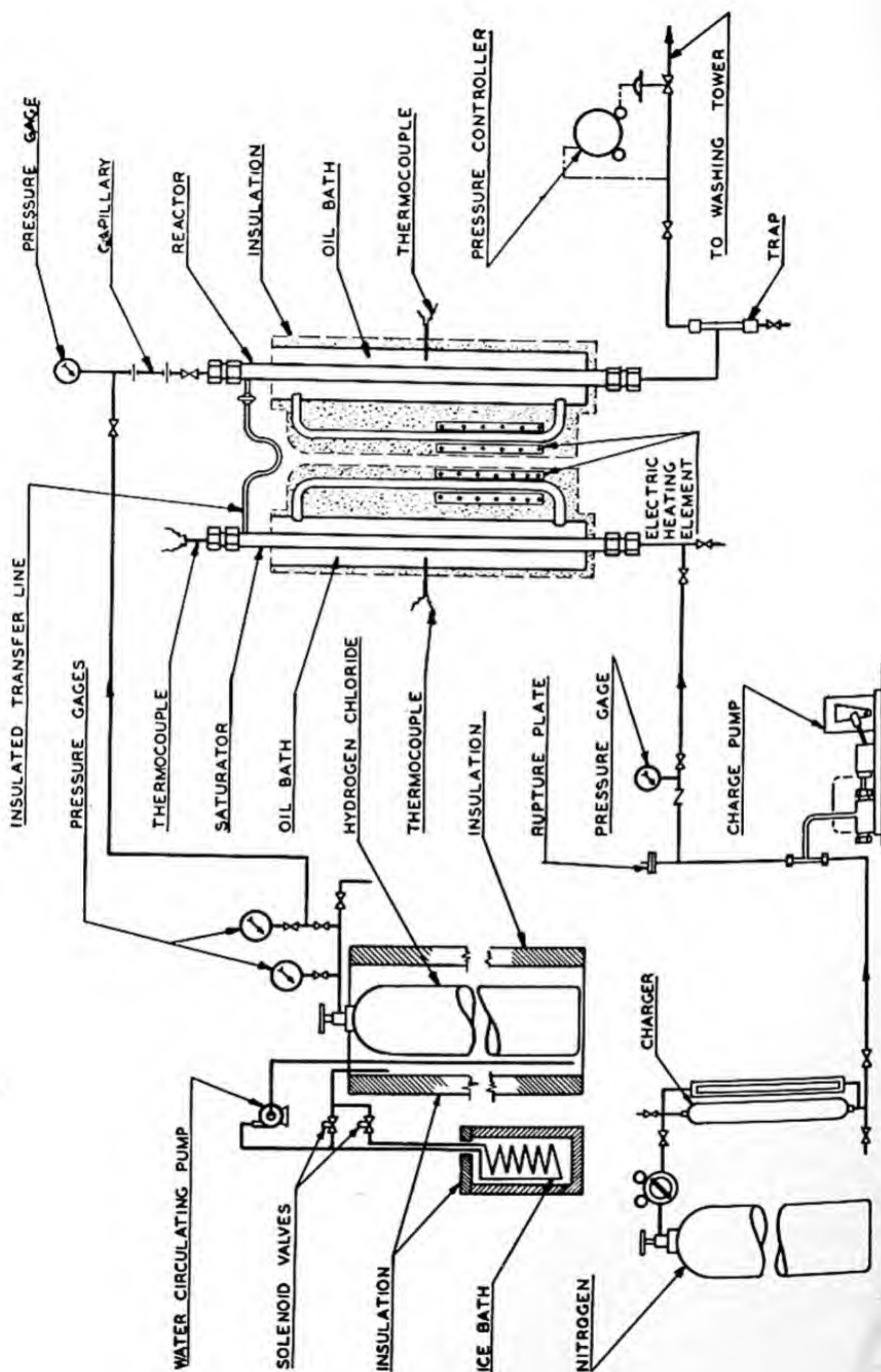


Fig. 2. Continuous isomerization unit.

of cracking as shown by the concentration of butanes in the product have been plotted against the percentage of benzene in the feed. The abscissa has been expanded to show better the effect of variations in benzene concentration in the low range by using a scale in which the distance from the

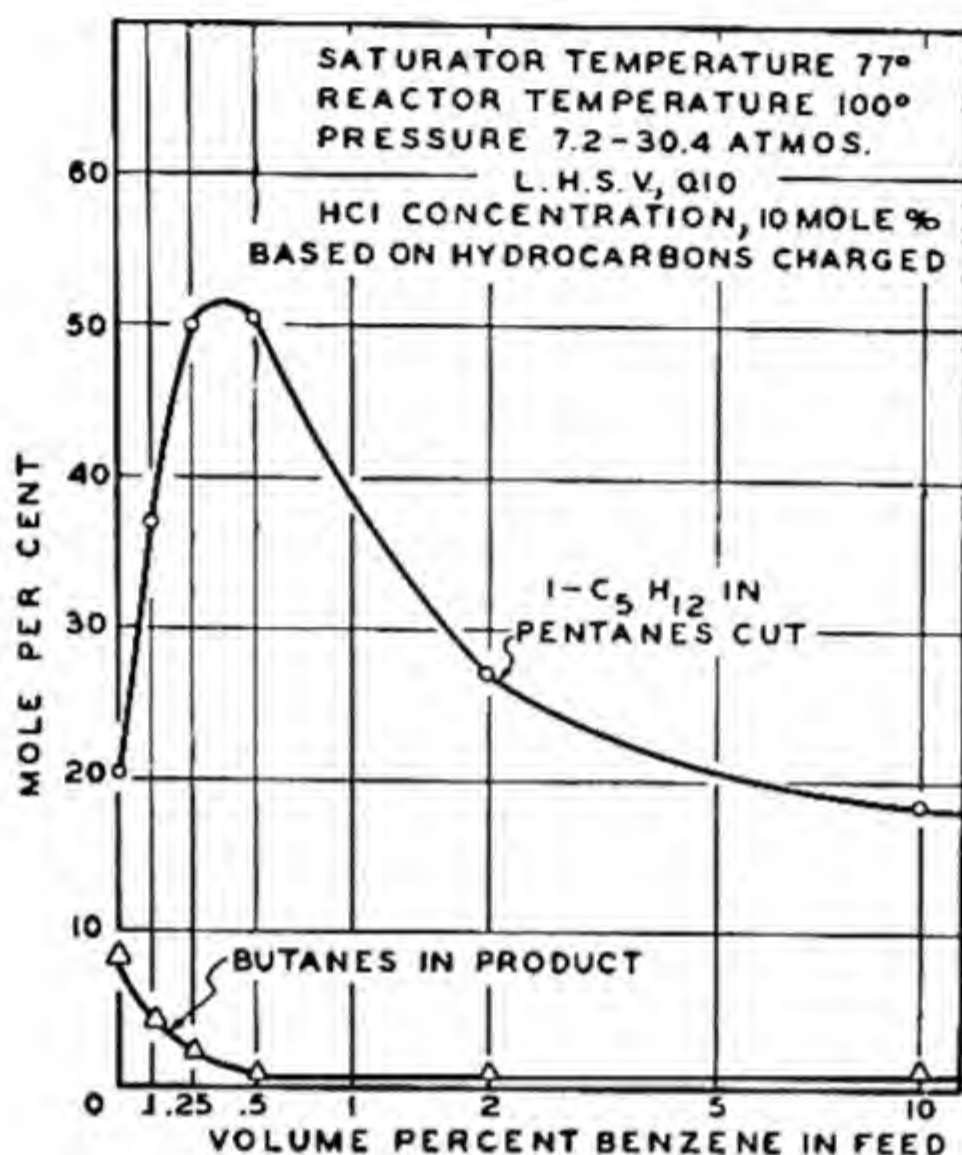


FIG. 3. Benzene as additive.

origin is proportional to $\log(v+1)$, where v is the volume % of benzene in the feed. Optimum isomerization was obtained with about 0.25 to 0.5 volume % benzene.

Thus, as increasing proportions of the additive were employed cracking was increasingly reduced. The isomerization reaction simultaneously became more selective and reached a peak at a point where cracking had become quite small. Further increase in additive concentration beyond this point gradually inhibited isomerization just as it inhibited cracking in the lower concentration range.

It was found that inhibition of isomerization by the higher benzene concentrations could be counteracted to some extent by a moderate increase in temperature but the optimum benzene concentration remained the same.

The life of aluminum chloride catalyst with 0.5 volume % benzene added to the pentane feed had been studied (Evering *et al.*, 31). This study was made in an autoclave which was charged with aluminum chloride, pentanes, hydrogen chloride, and benzene. Agitation was started and then

TABLE XXII

BATCH TESTS

Effect of Organic Additives upon the Isomerization of n-Pentane

Added compound		Mole % in product				
Name	Grams	i-C ₄ H ₁₀	n-C ₄ H ₁₀	i-C ₅ H ₁₂	n-C ₅ H ₁₂	C ₆ +
None	...	54.1	8.1	19.2	11.8	6.8
BENZENE AND n-ALKYLBENZENES						
Benzene	1.0	...	0.9	48.7	49.7	0.7
Toluene	1.0	...	0.7	50.7	48.0	0.6
Ethylbenzene	1.7	...	0.0	7.2	91.9	0.9
n-Propylbenzene	1.7	...	0.6	2.0	96.9	0.5
n-Butylbenzene	1.7	...	0.0	7.0	84.3	8.7
n-Amylbenzene	1.6	...	0.3	0.8	93.9	5.0
BRANCHED ALKYLBENZENES						
Isopropylbenzene	1.7	...	2.3	47.0	48.2	1.5
sec-Butylbenzene	1.5	2.0	1.6	43.5	50.1	2.8
tert-Butylbenzene	1.7	...	0.0	71.9	25.4	2.7
p-di-tert-Butylbenzene	1.7	3.0	0.2	35.0	60.9	0.9
POLYMETHYLBENZENES						
1,4-Dimethylbenzene	1.7	...	1.3	52.1	44.7	1.9
POLYCYCLIC AROMATIC HYDROCARBONS						
Biphenyl	2.0	2.5	0.1	31.5	65.1	0.8
Diphenylmethane	2.0	...	2.4	35.3	60.1	2.2
Naphthalene	2.0	8.5	1.0	56.1	30.7	3.7
2-Methylnaphthalene	2.0	5.7	0.4	37.1	52.3	4.5

DERIVATIVES OF AROMATIC HYDROCARBONS

Chlorobenzene	1.0	3.3	0.6	62.4	32.1	1.6
<i>p</i> -Chlorotoluene	2.1	25.3	0.9	58.0	9.0	6.8
<i>o</i> -Dichlorobenzene	1.7	50.7	7.7	19.6	11.8	10.2
<i>p</i> -Dichlorobenzene	2.0	49.1	5.4	26.3	9.8	9.4
Diphenyl ether	2.1	...	1.4	53.6	44.3	0.7
Diphenyl ketone	2.0	43.2	2.2	23.2	24.0	7.4
Aniline	2.4	43.7	2.3	26.7	13.8	13.5
Diphenylamine	2.0	49.4	4.7	25.3	18.3	2.3

NAPHTHENES

Cyclohexane	8.5	...	1.6	...	46.5	6.4
Methylcyclohexane	8.5	...	2.5	...	35.6	6.5
Ethylcyclohexane	8.7	...	0.0	...	40.2	2.5
Dimethylcyclohexanes	8.6	...	0.4	...	39.7	2.7
Isopropylcyclohexane	8.6	...	5.0	...	37.2	6.3
1,3- and 1,4-Methylethylcyclohexanes	8.7	...	2.8	...	49.3	2.4
<i>n</i> -Butylcyclohexane	8.8	...	12.0	...	43.0	8.7
<i>tert</i> -Butylcyclohexane	8.1	19.5	...	0.8	43.7	10.9
1-Methyl-4-isopropylcyclohexane	8.1	35.0	...	2.6	20.6	8.9
Diethylcyclohexanes	8.8	14.4	...	0.2	39.0	5.5
1-Ethyl-4-isopropylcyclohexane	8.8	22.3	...	2.8	42.0	8.0

Materials charged in each test were 85 g. *n*-pentane, 15 g. anhydrous aluminum chloride, 2.7 ± 0.4 g. anhydrous hydrogen chloride and the indicated additive. Conditions were 6 hours at 75° C. Maximum pressure developed ranged from 3.3 to 8.2 atmospheres.

TABLE XXIII

CONTINUOUS TESTS

Effect of Organic Additives upon the Isomerization of Pentane

Added Compound	Vol. % in feed	Pentane feed ^a	Test period hours ^b	Mole % in Product					
				<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₃ H ₁₂	<i>n</i> -C ₃ H ₁₂	C ₆ +	
None	...	B	72-84	...	8.3...	17.3	67.9	6.3	
BENZENE									
Benzene ^c	0.10	D	79-187	...	4.4...	33.6	57.2	4.8	
Benzene ^c	0.25	D	72-204	...	2.3...	47.3	47.2	3.2	
Benzene ^d	0.50	D	24-68	...	0.4...	49.0	48.1	2.6	
Benzene	2.0	D	24-60	...	0.3...	25.8	69.5	4.5	
Benzene ^c	10.0	D	48-84	...	0.5...	15.9	70.1	13.5	
NAPHTHENES									
Methylcyclopentane	10.0	B	48-60	...	0.3...	54.7	31.4	13.6	
Cyclohexane	5.0	B	60-72	...	3.9...	56.8	30.1	9.2	
Cyclohexane	10.0	B	48-60	...	1.4...	54.3	30.1	14.2	
Cyclohexane ^c	10.0	A	72-84	1.3	0.8	53.3	32.0	12.6	
Methylcyclohexane	10.0	B	24-60	...	1.7...	60.6	24.5	13.2	
Ethylcyclohexane ^c	5.0	C	120-168	...	0.3...	49.4	45.5	4.9	
Dimethylcyclohexanes ^c	5.0	C	36-132	...	0.4...	44.2	51.1	4.3	
Hydrindan ^c	5.0	C	36-120	...	0.0...	32.6	60.0	7.5	
Decahydronaphthalene	10.0	B	91-107	...	0.0...	19.2	67.1	13.7	
Bicyclohexyl	10.0	B	48-60	...	0.0...	4.5	80.9	14.6	

	PARAFFINS					
	Isobutane ^c	10.0	C	36-168	14.7	1.2
	Isobutane ^c	20.0	C	48-108	26.2	1.2
	n-Hexane	20.0	B	24-36	11.6	17.3
					47.0	6.8
					35.3	6.1
					50.4	20.7

Reactor conditions were unless otherwise indicated in subsequent footnotes, 34 atmospheres, 100° C., 0.10 LHSV (liquid hourly space velocity). HCl concentration 10 mole % on the hydrocarbons charged. Saturator temperature was 77°.

^a Commercial n-pentane feeds with the following compositions were used:

Feed	Composition, mole %		
	i-C ₃ H ₈	n-C ₃ H ₈	C ₄ +
A	5.5	94.4	0.1
B	0.0	95.4	4.6
C	10.0	86.9	3.1
D	7.4	91.1	1.5

^b Measured from start of indicated conditions.

^c The experiments were made at 17 atmospheres.

^d The experiments were made at 10.2 atmospheres.

the reaction mixture was quickly brought up to temperature. After a given time, agitation was stopped and the reaction mixture was quickly cooled. The aluminum chloride catalyst was allowed to settle and the bulk of the liquid product was withdrawn through a tube extending two-thirds of the way to the bottom of the reactor. The reactor was then recharged and the procedure repeated a number of times.

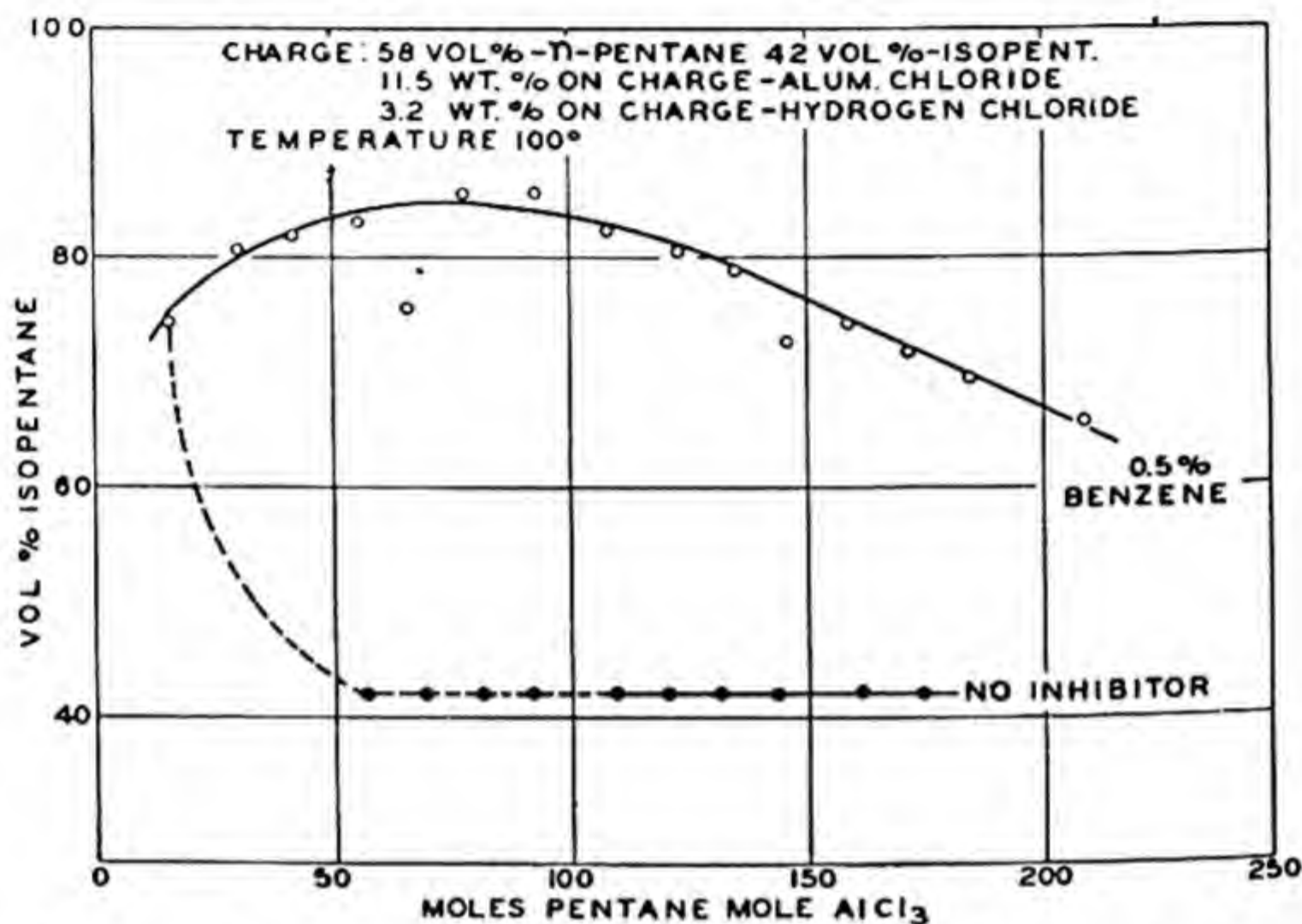


FIG. 4. Effect of benzene on catalyst life in pentane isomerization.

The results of these studies are given in Figs. 4 and 5. The benzene inhibited the disproportionation reaction; only 4% butanes were produced whereas the isomerization reaction proceeded readily. At a catalyst age of 212 moles pentane per mole aluminum chloride, the reaction product contained 66 volume % isopentane. In the absence of benzene the isomerization ceased after 55 moles pentane per mole aluminum chloride had been reacted.

At a catalyst age of 185 moles pentanes per mole aluminum chloride the benzene was omitted. There was little disproportionation at this point because the benzene remaining in the reactor was dissolved in the catalyst complex. However, in the subsequent run (also without benzene) at 198 moles pentane per mole aluminum chloride, a great deal of disproportionation was obtained, since a large proportion of benzene was extracted from the catalyst in a previous run. The inclusion of 0.5 volume % benzene in the following experiment again inhibited the disproportionation.

Substituted aromatics. A variety of different aromatic compounds

was investigated (Mavity *et al.*, 32). The results obtained with each of these, classified according to type, are included in Table XXIII. The data are limited to a single concentration with each additive.

Of the *n*-alkylbenzenes the effect of toluene equalled that of benzene. The higher alkylbenzenes inhibited both cracking and isomerization.

The branched alkylbenzenes exhibited considerable variation in behavior. With *tert*-butylbenzene the effluent contained 71.9 mole % isopentane, the highest concentration produced with any of the additives tested.

Results with 1,4-dimethylbenzene equalled those with benzene or toluene.

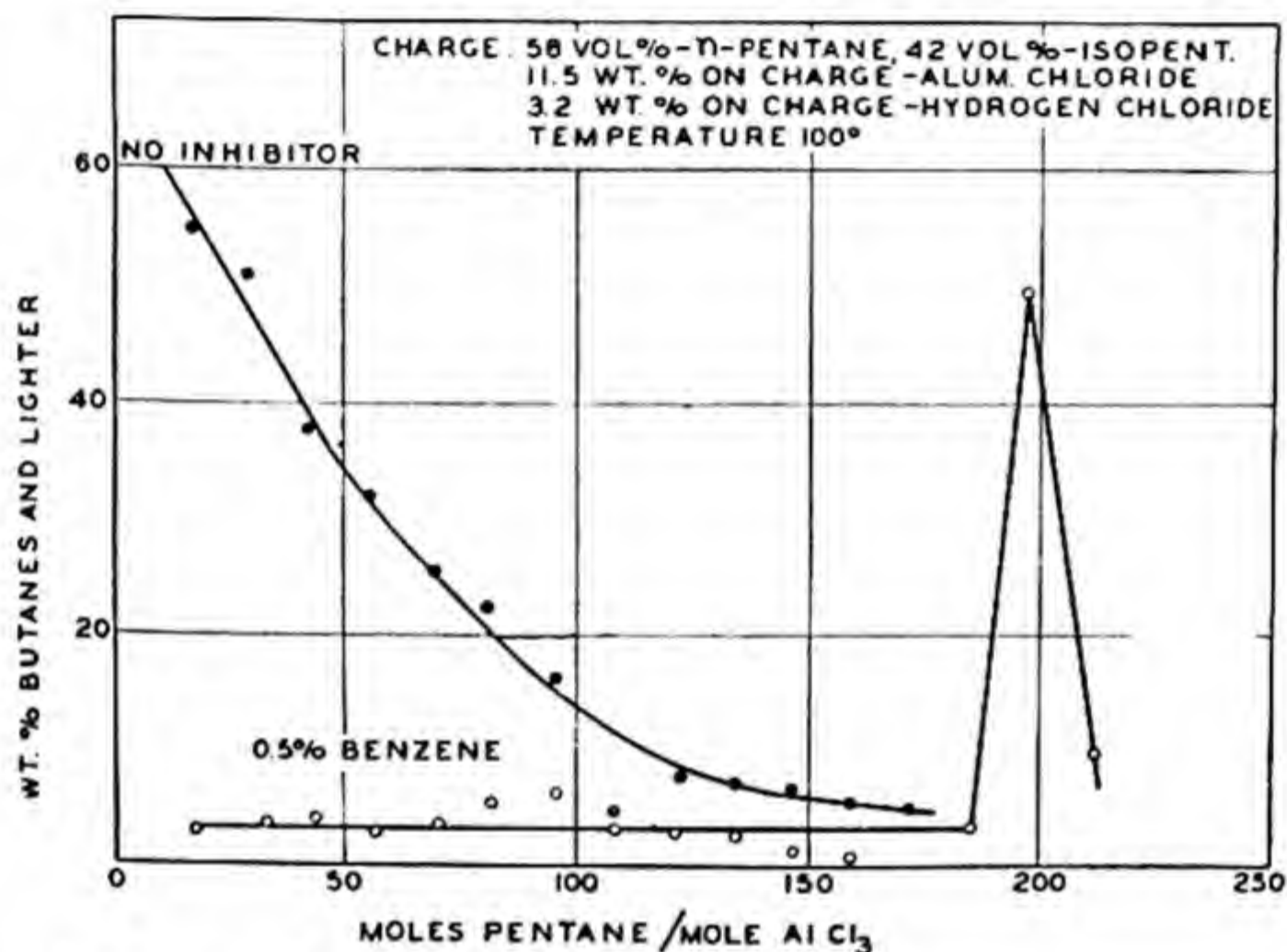


FIG. 5. Effect of benzene on disproportionation in pentane isomerization.

Several polycyclic aromatics exhibited positive inhibiting action.

Aromatic hydrocarbon derivatives which were quite effective as inhibitors are chlorobenzene and diphenyl ether.

(2) Naphthenes. Cyclohexane and the lower molecular weight mono- and disubstituted cyclohexanes used in concentrations of about 5 to 10% in the feed blends were quite effective in repressing cracking in favor of isomerization both in batch tests (Table XXII) and continuous operation (Table XXIII). The higher molecular weight members of the series containing substituents with a total of four or more carbon atoms were less effective for inhibiting cracking. In the continuous tests certain bi- and dicyclics repressed both cracking and isomerization.

The life of aluminum chloride catalyst in the presence of naphthenes

was investigated under the same conditions used in life studies where aromatics were used as inhibitors (Evering *et al.*, 31). The conversion to isopentane with 5.0% cyclohexane was slightly lower than with 0.5% benzene, but the catalyst life was slightly longer. Decreasing the cyclohexane content from 5.0% to 2.5% at a catalyst age of 195 moles pentanes per mole aluminum chloride resulted in the doubling of the disproportionation side reaction.

Careful fractionation carried out on samples (1 to 7 l.) of the effluent from the continuous runs with each naphthene and with benzene, showed that in all cases a major portion of the original additive was recovered as such or along with isomers. However, varying amounts of higher boiling products were usually recovered. With lower members of the naphthene series and with benzene these products were characterized as alkyl-naphthenes and alkylbenzenes respectively.

(3) Paraffins. In the presence of isobutane the extent of isomerization was somewhat greater than when no additive was used but there was also a net production of disproportionation products (Mavity *et al.*, 32). The effectiveness of isobutane in no way compares with that of cyclic hydrocarbons (Table XXII).

The straight chain paraffin, *n*-hexane, had no apparent effect on the reaction. This might be anticipated from the fact that its homologue, *n*-pentane, does not suppress its own decomposition. *n*-Butane was likewise not effective as an inhibitor of disproportionation.

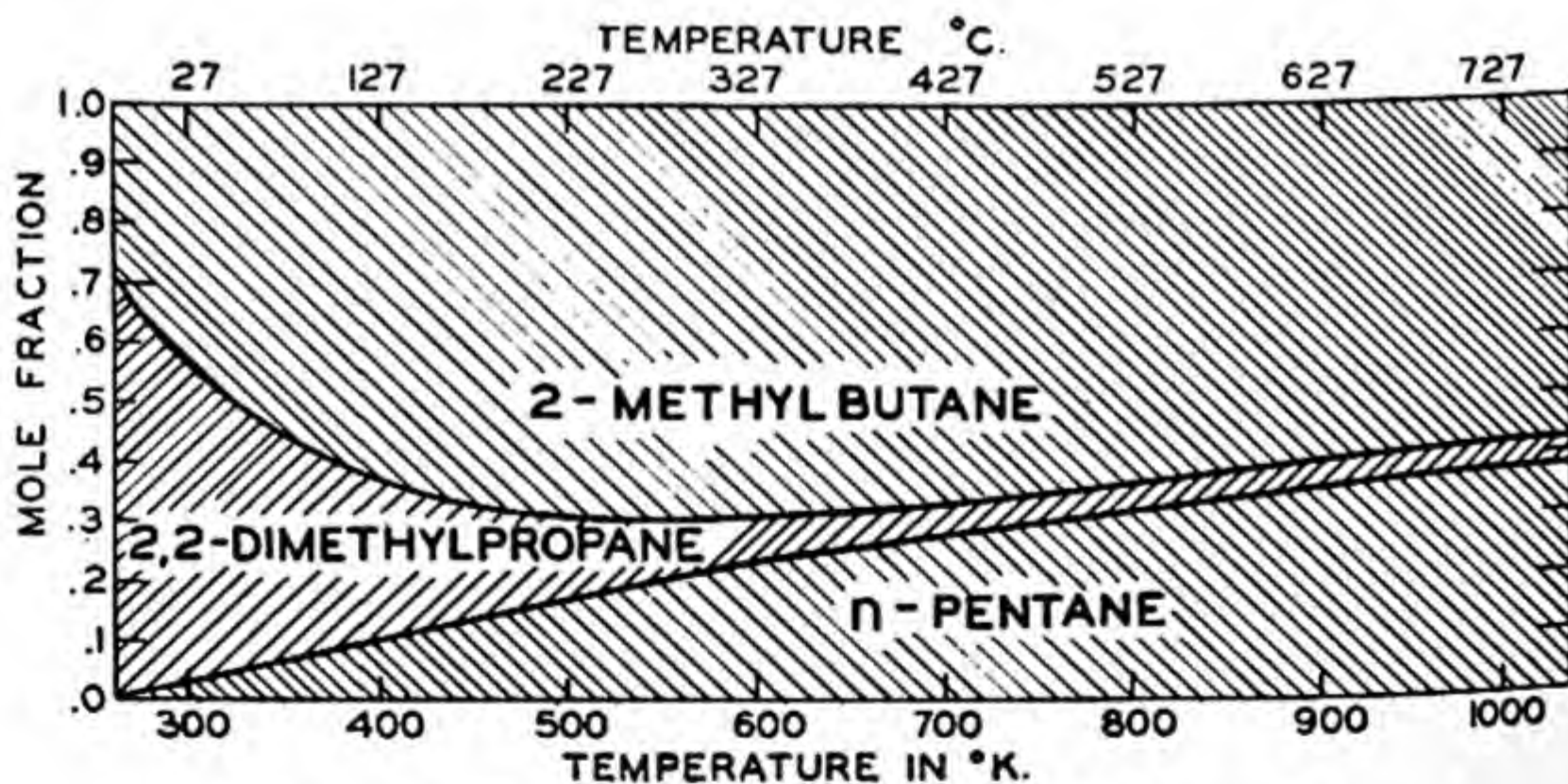


FIG. 6. Equilibrium concentrations of the pentanes.

3. Equilibrium Study of Pentanes

a. *Calculation of Equilibrium Concentration.* The equilibrium constants of *n*-pentane, isopentane and 2,2-dimethylpropane (neopentane), have

been calculated according to the method described in Section II, 3a. (Rossini, Prosen, and Pitzer, 12). The concentration of the three pentanes as a function of temperature is given in Fig. 6.

b. Experimental Determination of Equilibrium Concentration. The experimental determination of the equilibrium constants has been studied by various investigators.

The early study of the equilibrium constants of pentanes is open to criticism because the isomerization was accompanied by excessive decomposition (Moldavskii, Nizovkina, and Shterner, 33; Shuit, Hoog, and Verheus, 4). In order to establish the equilibrium constant, the isomerization from both the normal and the isopentane side was studied under experimental conditions designed to reduce to a minimum the amount of secondary reactions (Pines *et al.*, 13). On the basis of experimental results obtained the concentration of isopentane and *n*-pentane in liquid and vapor phase was calculated as a function of temperature; the formation of neopentane

TABLE XXIV
Isomerization of Pentanes

Temp. °C.	Mole % isopentane	
	Liquid	Vapor
60	87.6	89.6
70	86.8	88.6
80	86.1	88.1
90	85.3	87.3
100	84.6	86.5
110	83.9	85.7
120	83.2	84.9
130	82.5	84.1
140	81.9	83.4
150	81.3	82.6
160	...	81.9
170	...	81.1
180	...	80.4
190	...	79.7
200	...	79.0

was not observed. The results are summarized in Table XXIV. The calculated values were based on the equation

$$R \ln K_{G^0} = 1861/T - 1.299,$$

where K_{G^0} is the vapor phase equilibrium constant at zero pressure, T is the absolute temperature, and R is the gas constant. The value of 1861

cal./mole for the heat of isomerization of pentane is in good agreement with the value of 1930 cal./mole given by Rossini *et al.* (12).

Evering and d'Ouille (34) have also studied the equilibrium of normal and isopentane in the presence of cracking suppressors. At 100° they found that the equilibrium mixture in the gas phase consists of 78.5% isopentane, while Pines *et al.* (13) found the value of 81.9%. The reason for the difference between the two values is not known and further work will be necessary to resolve this discrepancy.

4. Mechanism of Isomerization

a. Chain Mechanism. It has been shown that the isomerization of saturated hydrocarbons is affected by various factors inherent in the usual type of laboratory technique employed, and by impurities present in the commercially available reagents (Pines and Wackher, 7, 8, 11, 23), (Pines, Abraham, and Ipatieff, 35). For this reason it is desirable for the study of the mechanism of the isomerization reaction, to deal with highly purified reagents; this is possible through the use of a high vacuum technique.

The study of the isomerization of pentanes, although dealing chiefly with commercial grades of reagents or C.P. grades that were not rigorously purified brought out several factors which seem to throw some light on the mechanism of isomerization.

The additives used for inhibiting the cleavage of pentanes during isomerization belong to either one or both of the three categories: (a) alkylatable inhibitors, such as aromatic hydrocarbons; (b) hydrogen donors such as decahydronaphthalene, or (c) molecular hydrogen itself. Compounds that can be alkylated and which are also known to act as hydrogen donors under certain conditions include isobutane, methylcyclohexane, and cyclohexane.

In order to obtain some conclusive data as to the course of isomerization, several experiments were made using highly purified reagents and a high vacuum technique (Mavity *et al.*, 32).

These experimental data, summarized in Table XXV show that aluminum chloride-hydrogen chloride caused a great deal of decomposition of *n*-pentane. The addition of a little benzene inhibited both isomerization and the cracking of *n*-pentane. The effect of benzene was pronounced even when the concentration of hydrogen chloride was increased from 1 to 7%.

These experiments indicate that benzene inhibits the cleavage of pentane; therefore carbonium ions, necessary for the isomerization of *n*-pentane to isopentane are not produced in sufficient amounts for isomerization (Section II, 4c(1)). The mechanism through which the inhibition

of the cleavage reaction proceeds is not entirely clear at present. Its complete clarification will require further experimental work carried out under strictly controlled conditions, including a study of the kinetics of the reaction.

The addition of water to a mixture composed of pentane, aluminum chloride, hydrogen chloride, and benzene causes the isomerization of *n*-pentane. This is not surprising, inasmuch as it was already shown (Section II, 2d) that hydroxyaluminum dichloride which is formed through the action of water on aluminum chloride is not equivalent to aluminum chloride-hydrogen chloride catalyst. The latter catalyst required an outside source of carbonium ions to catalyze the isomerization of *n*-butane to isobutane; hydroxyaluminum chloride probably forms the carbonium ions necessary for this reaction through halogen-hydrogen interchange between the catalyst and the alkane (Section II, 4c(3)).

The commercial aluminum chloride may contain enough hydroxyaluminum chloride to cause such an isomerization without the introduction of carbonium ions from an outside source. This is brought out in Table XXV, experiment 7, where the commercial grade of aluminum chloride was used as a catalyst.

TABLE XXV

Isomerization of n-Pentane Using High Vacuum Technique

Experiment No.	1	2	3	4	5	6	7
Temp., °C.	75	75	75	75	75	75	75
Time, hrs.	6	6	6	6	6	6	6
Charge, ^a moles							
<i>n</i> -Pentane	100	100	100	100	100	100	100
Aluminum chloride	9.4	9.4	9.5	9.5	9.4	9.5	9.4 ^b
Hydrogen chloride	0	1.09	1.1	7.4	7.3	7.4	7.4
Water	0	0	0	0	0.97	0.98	0
Benzene	0	0	1.17	1.17	0	1.16	1.17
Analysis, mole %							
Isobutane	...	47.1	52.5	2.8 } Trace	8.9
<i>n</i> -Butane	...	2.0	23.8		
Isopentane	0	22.1	0.3	0.1	14.0	46.2	
<i>n</i> -pentane	100	14.1	5.5	50.0	89.9
Hexanes and higher	...	14.7	4.2	1.0	1.2

^a These materials were rigorously purified except as indicated in *b*.

^b Commercial AlCl₃.

It was shown in Fig. 3 that with the increase in benzene concentration from 0.25 to 10% the degree of isomerization (including decomposition) decreases. In line with the experimental results obtained with the highly purified reagents, it is probable that in the presence of benzene the car-

bonium ions necessary to cause the isomerization of *n*-pentane to isopentane were obtained through the presence of small amounts of extraneous material. By increasing the concentration of benzene the chance for the carbonium ions to react with it is greatly increased; for that reason the concentration of carbonium ions available for causing the isomerization is decreased.

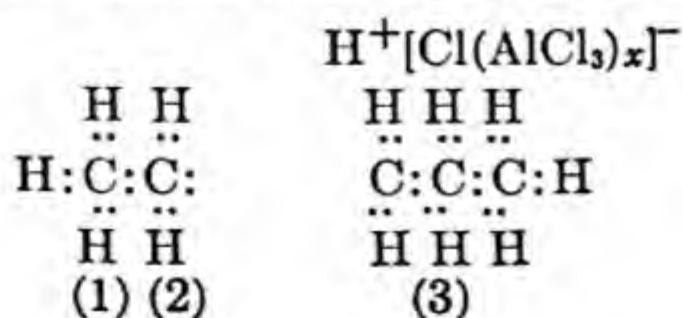
In order to obtain the same effect with naphthenes as with benzene, the concentration of the former has to be much greater. The reason for this seems to be that the interaction of a naphthene with a carbonium ion does not proceed as readily as with aromatic hydrocarbons.

It is interesting to note that in the case of polyalkylated aromatics, or those which are not readily alkylated, the degree of decomposition is relatively high, which is in line with the data reported.

2,2-Dimethylpropane (neopentane) which, according to the calculated equilibrium constants (Section III, 3a) ought to be one of the main constituents of the isomerization of pentanes at room temperature, has not been reported as present among the products of isomerization. This is not surprising in view of the proposed mechanism of isomerization (Section II, 4c) which involves the formation of carbonium ions. In order for neopentane to be formed, it is necessary that a neopentyl carbonium ion be produced, which, through a hydrogen transfer reaction, would yield neopentane; neopentyl carbonium ion, however, is very unstable and rearranges into a tertiary pentyl carbonium ion (Whitmore *et al.*, 36, 37).

The mechanism given above is merely a suggestion, based on presently available data, as to the function of the decomposition inhibitors in the isomerization of *n*-pentane. It is hoped that a systematic study of the kinetics of isomerization of saturated liquid hydrocarbons in the presence and absence of cracking suppressors, may furnish additional information about the mechanism of isomerization.

b. Mechanism of Evering, d'Ouille, Lien, and Waugh. This mechanism is similar to that postulated by Heldman (Section II, 4a) and Powell and Reid (Section II, 4b) with the exception that the formation of free carbonium ion is postulated to lead to the rupture of the carbon chain as in cracking or disproportionation (Evering *et al.*, 31). It is assumed that the actual catalyst in isomerization with aluminum halide is a strong acid resulting from the association of hydrogen chloride and aluminum chloride $[HCl \cdot (AlCl_3)_x]$. It is postulated that the proton (H^+) and an anion of this strong acid forms a loose association with a paraffin as pictured below:



The proton comes within collision distance of the $C_{(2)}$ atom of the pentane molecule. The net effect of the positive ion is to neutralize part of the electron negativity which leaves the $C_{(2)}$ atom with a somewhat more positive charge, which gives a driving force for shaking loose the $C_{(1)}$ atom minus its electrons in the form of a carbonium ion. The same action of the proton causes the hydrogen atom attached to the $C_{(3)}$ carbon atom to be loosened, minus its electron pair. This proton is attracted by the negative ion which is in a position close to the pentane molecule. With the pentane molecule activated in this manner, the driving force for rearrangement comes from the tendency to lose a proton from the $C_{(3)}$ carbon atom and a carbonium ion (CH_3^+) from the $C_{(2)}$ carbon atom. An intermolecular shift occurs whereby the carbonium ion migrates to the $C_{(3)}$ carbon atom and the proton from the acid becomes permanently bound to the $C_{(2)}$ carbon atom while the proton from the $C_{(3)}$ carbon atom goes to the anion, thus reforming from the strong acid catalyst $H^+ [Cl(AlCl_3)_x]^-$.

As long as the catalyst and hydrocarbon molecule remain closely associated, no cracking occurs. However, when molecular hydrogen is split out and the carbonium ion moves farther than some critical distance from the catalyst environment, then cracking does occur. This carbonium ion can pick off a hydrogen atom from an adjacent hydrocarbon molecule, thus stabilizing itself and forming another carbonium ion to propagate the chain; the carbonium ion can also lose a proton to form an olefin.

Another carbonium ion can react with the olefin thus formed to give a larger carbonium ion, which should be very unstable and crack into an olefin and another carbonium ion to propagate the chain. Since the olefins formed by cracking are susceptible to carbonium ion formation owing to the acid catalyst medium, this leads to a rapidly increasing carbonium ion concentration. This results in an accelerating chain reaction which leads to the promotion of a large amount of cracked products, unless the chain reaction is broken in the early stages.

According to this mechanism the cracking suppressors (Section III, 2), such as hydrogen or benzene react with carbonium ions before they set up a chain cracking reaction, thus stopping the chain.

The mechanism described above does not explain the fact that under controlled conditions, benzene in the presence of aluminum chloride-hydrogen chloride catalyst, inhibits not only the cracking but also the isomerization reaction (Table XXV, experiment 3) while in the absence of benzene cracking is the predominant reaction. The mechanism postulated above does not take into consideration the observations made that under controlled conditions saturated hydrocarbons such as methylcyclopentane, cyclohexane, or butanes (7, 23, 35) do not undergo isomerization, unless traces of olefins are present.

5. Commercial Methods for the Isomerization of *n*-Pentane

The following commercial methods were developed:

a. This process consists in passing pentane containing 0.2 volume % benzene and hydrogen chloride over aluminum chloride deposited on Porocel (Perry, 38). The following are the typical operating conditions and results obtained. Reactor conditions: temperature, 93°; pressure, 17 atmospheres; feed rate, 1.0 volume liquid hydrocarbon feed/volume Porocel/hour; hydrogen chloride concentration, 1.0 weight % (2.0 mole %) based on feed. Results: isopentane yield, 60%; selectivity, >99%; catalyst life, 120 gallons of isopentane/pound aluminum chloride or >18 gallons isopentane/pound of porocel.

b. This process consists in isomerizing pentanes and hexanes using a liquid aluminum chloride-hydrocarbon complex promoted with anhydrous hydrogen chloride. (Swearingen, Geckler, and Nysewander, 39). Hydrogen was added to repress cracking and maintain high catalyst activity. The conversion was accomplished by passing liquid hydrocarbon charge in a dispersed phase through the catalyst complex. The preferred reaction temperature was 115–122°; pressure, 48–55 atmospheres. Plants of 5000 barrels per stream day capacity have been successfully operated.

c. The catalyst employed is a molten salt mixture consisting of anhydrous aluminum chloride dissolved in antimony trichloride together with hydrogen chloride (McAllister *et al.*, 28). The process is carried out in a continuous manner; the spent aluminum chloride is continuously rejected and continuous catalyst make-up is employed in order to maintain the activity of the catalyst at a constant high level. The isomerization is carried out in the presence of hydrogen at a pressure of 20 atmospheres and at a temperature of about 90–110°. The conversion to isopentane per pass is of the order of 60%, and the consumption of catalyst is 1 pound of aluminum chloride per 100 gallons.

IV. ISOMERIZATION OF HEXANES

1. Without Cracking Suppressors

The action of aluminum halides on hexanes has been studied by many investigators (21, 40). It was reported that the reaction of aluminum chloride with *n*-hexane promoted with water yielded a hydrocarbon layer boiling at 25–76°, which appeared to contain some 2-methyl- and some 3-methylpentane, and a higher boiling fraction consisting of cyclohexane (Nenitzescu and Dragan, 41). The formation of the cyclohexane could not, however, be confirmed by subsequent work (Grummit *et al.*, 42); it is likely that *n*-hexane contained some cyclohexane or methylcyclopentane.

The product of the reaction of *n*-hexane with aluminum chloride and hydrogen chloride at reflux temperature consisted of isobutane and a mixture of paraffinic hydrocarbons boiling below and above *n*-hexane, of which one component appeared to be 2-methylpentane (Ipatieff and Grosse, 43).

The action of aluminum bromide on *n*-hexane using purified material and controlled conditions was studied (Grummit *et al.*, 42). In the absence of a promoter aluminum bromide does not isomerize *n*-hexane at room

temperature; this failure to react in the absence of a promoter is in agreement with previous work in which aluminum chloride was used as a catalyst (43). The effect of aluminum bromide-hydrogen bromide on *n*-hexane was studied by bubbling hydrogen bromide slowly through a solution of aluminum bromide in the *n*-hexane. The results obtained (Table XXVI) indicate that the isomerization of *n*-hexane is always accompanied by decomposition. The composition of the hydrocarbon layer was based on density, refractive index, and boiling point, and not on infrared analysis; for that reason the composition of the hydrocarbon layer is open to criticism.

TABLE XXVI

The Effect of Aluminum Bromide-Hydrogen Bromide upon n-Hexane

Experiment No.	1	2
Reagents used:		
<i>n</i> -Hexane, g.	310	272
Aluminum bromide, g.	51	74
Experimental conditions:		
Temp., °C.	Room	-20-0
Time, hrs.:	4	143
Product obtained:		
In Dry Ice trap, g.	25	...
Upper layer, g.	263 ^a	265 ^a
Lower layer, g.	66	62
Composition of upper layer, % ^b		
Isobutane	13.0	4.3
Isopentane	9.1	5.2
2,2-Dimethylbutane	1.8	9.6
2,3-Dimethylbutane	1.9	3.8
2-Methylpentane	5.5	10.4
3-Methylpentane	0.7	0.6
<i>n</i> -Hexane	57.2	64.5
Heptanes	7.8	...
Higher hydrocarbons	3.6	1.1

^a After washing and drying.

^b Includes the liquid in the Dry Ice trap.

The isomerization of branched chain hexanes in the presence of aluminum bromide-hydrogen bromide has been studied (Bishop, Burk, and Lankelma, 44). The summary of the results obtained, given in Table XXVII, shows that both 2-methylpentane and 3-methylpentane can isomerize with but a trace of cracking. The effect of reaction time on the conversion of 3-methylpentane shows two points of interest: the five-fold increase in cracking with the longer reaction time and the marked change in the relative concentration of the hexanes. It was found that 2,2-dimethyl-

TABLE XXVII
Effect of Aluminum Bromide-Hydrogen Bromide upon Branched Chain Hexanes

Experiment No.	1	2	3	4	5	6	7
Reagents used: Hexanes, kind							
Aluminum bromide, wt. %							
Experimental conditions:							
Temp., °C.							
Time, hrs.							
Conversion, %							
Composition of upper layer, %							
Isobutane	1.1	6.8	1.8	1.3	10.6
Isopentane	1.4	23.3	8.0	3.2	26.9	0.1	19.3
2,2-Dimethylbutane	1.4	11.5	79.5	4.6	14.5	6.8	18.7
2,3-Dimethylbutane	10.0	7.2	^a	17.5	10.0	74.9	4.0
2-Methylpentane	60.8	17.2	...	50.3	18.7	12.3	6.9
3-Methylpentane	17.6	8.4	...	17.0	9.0	...	3.2
Heptanes and higher	7.7	25.6	6.1	6.2	20.1	6.0	37.4

^a Unidentified hexanes 4.6%

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butane is not appreciably isomerized. The composition of the liquid product was based on physical constants only, and not on infrared analysis.

2. Cracking Suppressors

It has been shown that the hexanes behave in many respects in a manner similar to pentanes, namely the isomerization is accompanied by decomposition, which can be inhibited by hydrogen and organic additives (Evering *et al.*, 31). Thirty-four atmospheres hydrogen pressure was below the minimum effective pressure for inhibiting cracking in the isomerization of 2,3-dimethylbutane at 156°. One per cent cyclopentane had no effect on the inhibition of side reactions in combination with hydrogen, whereas the addition of 10% cyclopentane to the 2,3-dimethylbutane under the same conditions reduced the formation of butanes from 30 to 2.2%. The experimental results are given in Table XXVIII.

TABLE XXVIII

Effect of Hydrogen and Cyclopentane on the Conversion of 2,3-Dimethylbutane

Experiment No.	1	2	3	4
Reagents used:				
2,3-Dimethylbutane, ml.	700	1000	990	890
Cyclopentane, vol. %	1.0	10.0
Aluminum chloride, g.	50	73.6	69.0	69.0
Hydrogen chloride, g.	15	20.5	20.5	20.5
Hydrogen, atm.	68	34	34	34
Experimental conditions:				
Temp., °C.	100	156	157	160
Contact time, min.	20	10	10	10
Weight % of condensibles	0.5	32.6	30.0	2.0
Analysis of liquid product, vol. %				
2,2-Dimethylbutane	4.4	8.9	...	21.6
Pentanes	0.2	41.5	...	5.1
2,3-Dimethylbutane	46.9	4.5	...	6.3
2-Methylpentane	31.6	14.4	...	37.8
3-Methylpentane	16.6	7.3	...	11.9
n-Hexane and higher	0.3	22.5	...	11.3
Cyclopentane	6.0

3. Equilibrium Study of Hexanes

a. Calculation of Equilibrium Concentration. The equilibrium constants of the hexanes were calculated from the heat of combustion as described in section II, 3a (Rossini, Prosen, and Pitzer, 12). The concentration of the five hexanes as a function of temperature is given in Fig. 7.

b. Experimental Determination of Equilibrium Constant. The experimental equilibrium constants for the isomeric hexanes were studied in an autoclave, which was mechanically stirred (Evering and d'Ouille, 34).

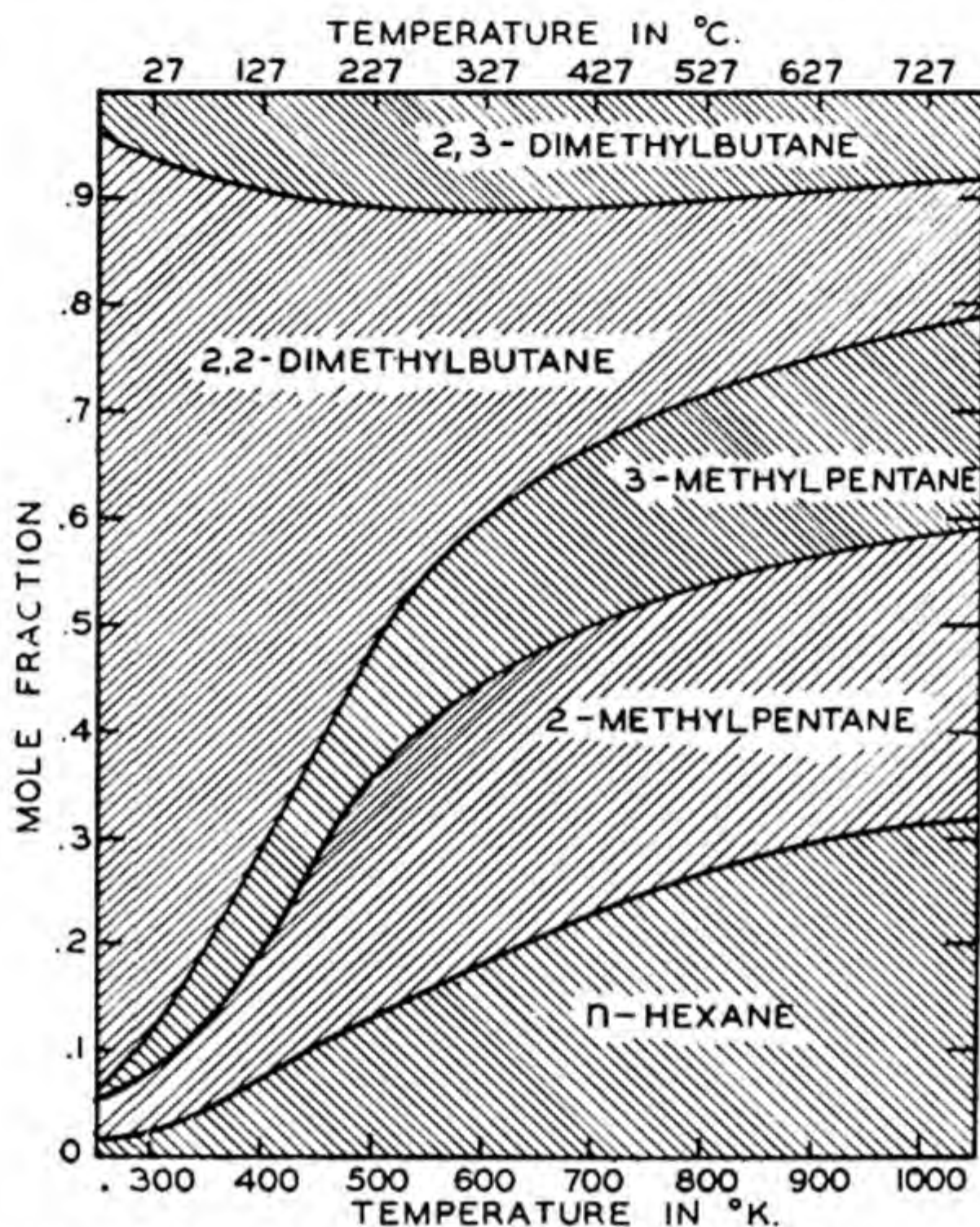


FIG. 7. Equilibrium concentrations of the hexanes.

The hydrocarbon used in this investigation was a Mid-Continent naphtha having the composition given in Table XXIX.

TABLE XXIX

Composition of Mid-Continent Light Naphtha

	Volume %
Isopentane	1.5
<i>n</i> -Pentane	35.4
Cyclopentane	3.0
2,2-Dimethylbutane	1.0
2,3-Dimethylbutane	1.0
2-Methylpentane	23.3
3-Methylpentane	13.4
<i>n</i> -Hexane	17.4
C ₆ naphthenes	3.0
Benzene	0.5

Although the hydrocarbon feed contained a considerable amount of material other than hexanes in the form of pentanes, naphthenes, and a small amount of aromatics, they were not believed to have any detrimental effect on the equilibrium of hexanes. In fact, the naphthenes and benzene served the useful function of being decomposition inhibitors, thus reducing side reactions.

The experiments were made as follows: 72 g. aluminum chloride or its equivalent as aluminum chloride-hydrocarbon complex were placed in the reactor, usually with 1 l. naphtha, and sealed into the reactor. Hydrogen was added in the higher temperature runs until the total reactor pressure was 41 atmospheres at room temperature. In experiments at 21°, anhydrous aluminum bromide was used as the catalyst in an effort to establish the equilibrium more rapidly.

The equilibrium constants for hexanes were determined at 21, 102, 161, and 204°. Since the contents of the reactor were cooled to room temperature before removal, the analyses reported in Table XXX are for the

TABLE XXX
Composition of Reactor Contents at Equilibrium

Temp., °C.	21	102	161	204
<i>Moles</i>				
Hydrogen785	.900
Hydrogen chloride	.310	.356	.493	.246
Propane	.010	.055	.020	.121
Isobutane	.360	.920	.382	.714
<i>n</i> -Butane	.044	.324	.232	.223
Isopentane	2.600	2.325	2.515	1.841
<i>n</i> -Pentane	.463	.414	.815	.768
Cyclopentane	.209	.300	.271	.131
2,2-Dimethylbutane	2.295	1.400	.936	.538
2,3-Dimethylbutane	.386	.367	.346	.220
2-Methylpentane	.879	1.005	1.341	.928
3-Methylpentane	.342	.477	.671	.440
<i>n</i> -Hexane	.167	.336	.419	.349
Methyleyclopentane	.035	.173	.278	.200
Cyclohexane	.573	.352	.272	.120
Vapor: liquid ratio (at reactor temp.)	liquid	.006	.75	vapor
Mole % decomposition	5.0	15.3	7.4	15.9

combination of the vapor and liquid phase which existed at reaction conditions. The true equilibrium values for the hexanes in the vapor and liquid phase were calculated from these data by finding the vapor and liquid composition that existed in the reactor at the experimental temperature and pressure (Table XXXI).

TABLE XXXI

Equilibrium Composition of the Isomeric Heranes

Run No.	Composition	Temp. °C.	Reactor pressure atmospheres	Vapor-liquid ratio	Observed analysis mole %	Liquid mole %	Equilibrium Vapor mole %
1	2,2-Dimethylbutane	21	3.4	liquid	56.4	56.4	66.4
	2,3-Dimethylbutane	9.5	9.5	.82
	2-Methylpentane	21.6	21.6	16.9
	3-Methylpentane	8.4	8.4	6.0
	<i>n</i> -Hexane	4.1	4.1	2.5
2	2,2-Dimethylbutane	102	15.0	0.006	39.1	39.1	45.0
	2,3-Dimethylbutane	10.2	10.2	9.8
	2-Methylpentane	28.0	28.0	26.3
	3-Methylpentane	13.3	13.3	11.7
	<i>n</i> -Hexane	9.4	9.4	7.2
3	2,2-Dimethylbutane	161	59.5	0.75	25.2	24.9	25.9
	2,3-Dimethylbutane	9.3	9.1	9.7
	2-Methylpentane	36.1	36.4	35.5
	3-Methylpentane	18.1	18.2	17.8
	<i>n</i> -Hexane	11.3	11.4	11.1
4	2,2-Dimethylbutane	204	73.5	vapor	21.7	...	21.7
	2,3-Dimethylbutane	8.9	...	8.9
	2-Methylpentane	37.5	...	37.5
	3-Methylpentane	17.8	...	17.8
	<i>n</i> -Hexane	14.1	...	14.1

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The agreement between the experimental values and those calculated from heats of combustion are good for *n*-hexane and 2,3-dimethylbutane but are in disagreement on 2,2-dimethylbutane and the methylpentanes. The temperature coefficient for all the isomers is in good agreement but the

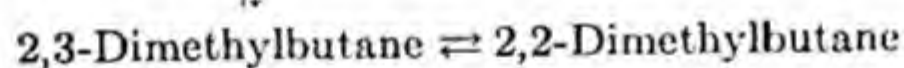
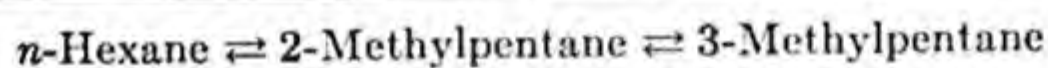
TABLE XXXII

Effect of Decomposition on Hexane Equilibrium

<i>Hydrocarbon</i>	<i>2,3-Dimethylbutane</i>	<i>2,3-Dimethylbutane</i>
Cyclopentane, vol. %	8.3	0.0
Aluminum chloride, g.	69.0	73.6
Hydrogen chloride, g.	20.5	20.5
Contact time, min.	10	10
Temp., °C.	160	156
H ₂ pressure, atm.	37.5	37.5
Vol. % decomposition to lighter than C ₆	7.4	62.9
Analyses of Hexanes, vol. %		
2,2-Dimethylbutane	22.6	21.8
2,3-Dimethylbutane	8.8	11.0
2-Methylpentane	37.3	35.2
3-Methylpentane	18.3	17.8
<i>n</i> -Hexane	13.0	14.2

TABLE XXXIIA

Scheme of Stepwise Isomerization of Hexanes



<i>Isomerization reaction</i>	<i>Isomerization velocity "K"</i>
<i>n</i> -Hexane → 2-methyl- and 3-methylpentane	1.8
2-Methylpentane → <i>n</i> -hexane	0.7
2-Methylpentane → 3-methylpentane	150
3-Methylpentane → 2-methylpentane	65
2-Methylpentane → 2,3-dimethylbutane	6.0
2,3-Dimethylbutane → 2-methylpentane	3.9
2,3-Dimethylbutane → 2,2-dimethylbutane	0.8
2,2-Dimethylbutane → 2,3-dimethylbutane	0.04

heats of combustion predicted more 2,2-dimethylbutane than has been found experimentally. Aside from the absolute value there was a good agreement in the ratio of 2-methylpentane to 3-methylpentane.

The side reactions occurring during the isomerization of hexanes have no effect on the chemical equilibrium. This is shown in Table XXXII.

A study of the behavior of the individual hexane isomers under controlled conditions was made wherein the per cent conversion was varied over a wide range (Evering and Waugh, 44a). By plotting conversion against the per cent of the various hexane isomers in the product (based on 100% converted) and extrapolating back to zero per cent conversion an insight into the primary and secondary reaction products was obtained. From the experimental data it was postulated that the hexanes isomerize in a stepwise manner according to the scheme in Table XXXIIa. The indicated isomerization steps do not take place with equal ease. Isomerization rates for the various hexanes to the specific isomers have been calculated in terms of the specific reaction velocity "*K*" based on the assumption that the isomerization follows a first-order reaction law.

4. Commercial Methods for Isomerization of Hexane

Refer to section III, 5b.

V. ISOMERIZATION OF HEPTANES AND HIGHER ALKANES

1. Without Cracking Suppressors

The results of the many studies made on the action of aluminum halides on heptanes and their homologues indicate that the reaction requires a promoter such as hydrogen halide and that it is accompanied by the formation of two layers; the upper layer consists of paraffinic hydrocarbons and the lower layer of addition compounds between the aluminum halide and complex highly unsaturated hydrocarbons. The paraffinic hydrocarbons that result from this reaction contain a large proportion of lower boiling hydrocarbons, the latter consists mainly of isobutane and isopentane.

Extensive cracking occurred when aluminum chloride was added in small portions to a batch of heptane which was kept boiling, while the lower products of the reaction (which include any isomeric heptanes) were continuously removed through a fractionating column (Calingaert and Beatty, 45). The identification of the hydrocarbons formed was based on the determination of the physical constants. An estimation of the products obtained is given in Table XXXIII, which shows that only 5% of the resulting hydrocarbons consisted of isomeric heptanes.

The action of aluminum bromide on *n*-heptane, using highly purified materials and controlled conditions, has been studied (Grummitt *et al.*, 42). Aluminum bromide, rather than aluminum chloride, was selected as a catalyst because its hydrocarbon solubility permits the initial reaction to be homogeneous. The reaction was carried out in a flask which was evacuated, flamed, and rinsed dry with oxygen-free nitrogen. The aluminum bromide

was distilled into the reaction flask under diminished pressure. The hydrocarbon, after drying with phosphorous pentoxide, was distilled also into the reaction flask. The aluminum bromide dissolved in the hydrocarbon without sign of reaction. Hydrogen bromide was then bubbled

TABLE XXXIII

Products of Reaction of Aluminum Chloride on n-Heptane

	%
Pentanes and below	64.6
Hexanes	5.8
2,4-Dimethylpentane	1.5
2,2,3-Trimethylbutane	0.5
3,3-Dimethylpentane	0.4
2-Methylhexane	1.2
3-Methylhexane	1.6
Polymerization products	24.4

The yields were calculated on the basis of 100 parts *n*-heptane reacted.

slowly through the solution; as the reaction proceeded gas was liberated and a lower liquid layer formed. At the close of the reaction, the upper liquid layer was removed from the reaction flask by vacuum distillation. Table XXXIV summarizes the treatment of *n*-heptane with aluminum bromide.

TABLE XXXIV

Summary of Aluminum Bromide Treatment of n-Heptane

Experiment No.	1	2	3	4	5	6
Time, hrs.	14.5	3.7	2.5	4	7.5	7.3
Temp., °C.	100	32	25	23	24	25
Charge: mole %						
<i>n</i> -Heptane	94.8	95.2	88.5	90.1	85.9	83.7
Aluminum bromide	5.2	4.2	8.5	5.2	8.6	12.5
Hydrogen bromide	0	0.6	3.0	4.7	5.5	3.9
Results:						
% Conversion to lower layer	0.01	0.09	4.2	4.3	4.6	6.0
% Conversion, total	0.14	13.7	40.3	52.9	65	91.7

In the absence of a promoter, aluminum bromide had no appreciable effect upon *n*-heptane at temperatures up to the boiling point of *n*-heptane. Using hydrogen bromide as a promoter, reaction occurred readily at a temperature as low as -20° . At room temperature and higher, cracking was the principal reaction. The conversion to lower boiling products was

approximately from three to four times as great as the conversion to products boiling higher, which indicates that the principal reactions were cracking and isomerization. Of the two butanes, only isobutane was found in the products of reaction. Analysis of the liquid hydrocarbon fractions by distillation and physical constants showed that 2-methylhexane was present in the largest amount and 2,4-dimethylpentane, 2-methylpentane, 2-methylbutane, 2,3-dimethylbutane, 3-methylpentane, 2,2-dimethylbutane, and 3-methylhexane were present in descending order of abundance.

Although cycloparaffins have been reported (Nenitzescu and Dragan, 41) among the products of the action of aluminum chloride on *n*-heptane, subsequent work could not confirm this observation (42, 45).

2. Cracking Suppressors

The action of hydrogen upon *n*-heptane was studied in a rotating autoclave (Ipatieff and Schmerling, 30). It was found that hydrogen had a

TABLE XXXV
Action of Aluminum Chloride on n-Heptane

Experiment ^a No.	1	2	3	4	5
Atmosphere	N ₂	H ₂	H ₂	H ₂	H ₂
Reactants, g.					
<i>n</i> -Heptane	100	103	102	101	102
Aluminum chloride ^b	10	10	10	10	10
Hydrogen chloride	0	0	0	6	5
Pressure atm. at room temperature					
Initial	100	100	100	100	100
Final	100	100	100	75	100
Recovered catalyst, g.	18	15	16	15	17
Composition of liquid mole %					
Propane	3.2	2.5	...	20.6	7.2
Butanes	18.6	16.6	21.2	47.5	12.0
Pentanes	20.8	11.3	15.2	21.3	9.0
Hexanes	0.5	1.7	11.1	8.3	6.2
Heptanes	50.5	61.4	45.0	2.3	62.1
Octanes and higher	6.4	6.5	7.5	0.0	3.5
Moles alkanes formed per mole heptane charged	1.10	1.05	1.01	1.48	0.94

^aExperiments carried out in glass liners in a rotating, 850-cc. autoclave. The autoclave was heated at 150° for 4 hours.

^bResublimed aluminum chloride was used.

different effect on the action of aluminum chloride on heptanes and higher molecular weight hydrocarbons than on pentane and hexanes. With pure aluminum chloride, in the absence of added hydrogen, *n*-heptane underwent autodestructive alkylation at 150° regardless of whether the reaction was

carried out under hydrogen or under nitrogen pressure. On the other hand in the presence of added hydrogen chloride and under hydrogen pressure, destructive hydrogenation occurred to give a high yield of lower boiling products, particularly isobutane; under nitrogen pressure the heptane was autodestructively alkylated. When autodestructive alkylation occurred, the number of moles of alkane produced per mole of heptane was about 1.0–1.1; a substantial amount of octane and higher boiling material was produced. In the case of destructive alkylation very little product of higher molecular weight than heptane was produced, and the yield of alkanes per mole of heptane reacted was about 1.4–1.5 moles (Table XXXV).

The use of hydrogen with heptane did not completely prevent the formation of a catalyst layer complex regardless of conditions, however, the complex which was obtained in its presence contained less hydrocarbon and was more active as indicated by the heat evolved by its reaction with water. The catalyst layer formed under nitrogen pressure was a brown tar.

The action of aluminum chloride on higher molecular weight alkanes, e.g., those obtained from carbon monoxide hydrogen synthesis and boiling between 100–200°, was analogous to its action on *n*-heptane.

The foregoing study indicates that, unlike *n*-pentane and hexanes, hydrogen does not suppress the formation of side reactions during the action of aluminum chloride on *n*-heptane and higher alkanes.

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The Application of X-Ray Diffraction to the Study of Solid Catalysts

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PART I. DESCRIPTION OF METHODS

I. INTRODUCTION

In this discussion of x-rays and catalysis, no attempt will be made to review critically the extensive literature dealing with the subject. Such extensive reviews have been presented by others, notably by Prof. W. O. Milligan at Gibson Island in 1944. Rather, a general discussion of the techniques of x-ray diffraction applicable to the study of catalysis will be presented followed by a few specific applications of these methods as carried out by the authors and their colleagues.

Practically all x-ray scattering experiments are similar in principle. A

well-defined beam of monochromatic or nearly monochromatic x-rays is allowed to fall on a specimen. A part of this radiation is scattered in all directions and is recorded by some device such as a photographic film, ionization chamber or Geiger counter. The pattern of scattered radiation is determined by the geometry of the experimental set up and by the scattering specimen. Because the structure of the specimen is one determining factor, one may be tempted to set up a one-to-one correspondence between the pattern recorded and the specimen structure. However, while the pattern of scattered x-rays can be predicted from the structure of the specimen, the reverse proposition is not true. Only sometimes (rarely for complex structures) can the structure of the specimen be determined from the x-ray scattering. Nevertheless, much useful information can be obtained from the x-ray diagrams.

II. THE PURPOSE OF X-RAY WORK

Most of the diffraction work done in the field of catalysis has been done using the powder method. This technique will be discussed from three standpoints; namely, identification, orientation (principally electron diffraction) and angle of scatter.

1. Identification

(a) Identification by x-ray diffraction uses Bragg's Law relating the interplanar spacing in crystalline materials with the x-ray wavelength utilized and the sine of the angle of incidence of the x-ray beam and the crystal plane being considered. The significance of Bragg's law is that by suitably monochromatizing the x-rays the only two variables remaining are the interplanar spacing and the angle of scatter. As the latter can be easily determined from the geometry of the camera or other recording apparatus, the determination of the interplanar spacing is a simple and straightforward calculation.

(b) The powder method has its greatest use because of the fact that, theoretically, each crystalline material should give a unique diffraction pattern which would permit one to distinguish it from all other substances. Unfortunately, from a practical viewpoint, this uniqueness may be very difficult to recognize, especially in the field of catalysts. Catalysts are usually, but not always, finely divided substances, and accordingly yield poor diffraction diagrams with fuzzy, smeared maxima. In fact, in many a catalyst study, one can eliminate substances from further consideration as potential catalysts merely because they yield sharp diffraction diagrams of well-crystallized compounds. Because of this tendency toward poor diagrams, identifications may not always be clean-cut and unequivocal.

Thus, many of the forms of gamma-alumina existing between the lowest temperature form and alpha-alumina are hard to characterize. Another effect that can be misleading in the study of catalysts consisting of various solid components is the masking of components even though physical mixtures in the same proportions clearly show all the components. Two cases that immediately come to mind are the complete absence of the lines of molybdenum trioxide when it is present in quantities as high as 12% by weight on gamma-alumina in a hydroforming catalyst, and the nondetection of gamma-alumina when adsorbed on the surface of silica gel until it comprises about one-quarter the weight of the catalyst.

2. Orientation

When a specimen has no particular orientation (for example, a randomly oriented mass of small crystals, as in a powder), each reflection is spread out into a right circular cone of radiation whose axis is the x-ray beam. The intersections of these cones with the photographic films are the Debye-Scherrer powder lines. If, however, the crystals are not randomly distributed but lie in preferred orientations, the powder rings become nonuniform in density, indicating orientation. One of the outstanding studies of orientation in the field of catalysis was that of Beeck (1) who showed by electron diffraction that nickel films deposited under certain conditions showed unusual catalytic activity and that this activity was accompanied by a particular orientation of the nickel crystals.

3. Angle of Scatter

In the earlier applications of x-ray diffraction to catalyst study, the pattern of scattered radiation was determined for angles of 5° or more and the analyses consisted mainly of the usual Bragg's law application to determine the interplanar spacings of the samples under study. Scattering at small angles, i.e., at angles less than about 2° , has been studied more recently following Guinier's (2) verification of Debye's (3) prediction that scattering of a continuous nature should appear at these angles for certain types of materials. This continuous small angle scattering is different in character and in its theoretical interpretation from Bragg scattering. For the appearance of scattering effects of this type it is not necessary that any periodic structure be present in the specimen, nor is it even necessary that the material be crystalline. All that is required is that *large scale* discontinuities be present in the materials such as discontinuities in the electron density (or refractive index for x-rays). These generally arise from discontinuities in density. If regions of suitable size bounded by such discontinuities are present, then a continuous small angle scattering will be observable. The intensity of the scattering, will among other things, de-

pend on the magnitude of the change in the refractive index across the discontinuities, while the rate of change with the angle of scattering will depend on the size and shape of the regions.

III. TECHNIQUES

1. Specimen Preparation

The preparation of specimens for Debye-Scherrer powder diagrams has been adequately discussed in the literature and is fairly well standardized, coated fibers, extruded rods, or filled capillaries of glass, cellophane or of similar amorphous materials have been used (Bragg, 4; Jellinek and Fankuchen, 5).

2. Cameras

The cameras normally used for powder diffraction are also well standardized by the manufacturers of x-ray equipment and it is only an occasional special problem that will require an unusually designed camera such as an asymmetric focusing type or a special small angle scatter camera. Even these cameras are now commercially available.

3. Monochromators

To those familiar with powder work, monochromators usually represent a fine tool which is seldom called into use. The reason for the tendency to avoid crystal monochromatized radiation is that excessively lengthy exposure times have to be used. This shortcoming however, is not always decisive and is often more than compensated for by the value of the results obtained. The very lengthy exposures encountered can frequently be greatly shortened by proper adjustment and camera design.

(a) Plane crystal monochromators are usually made from crystals having a reflection with a large structure factor, i.e., high intensity, from one of its cleavage planes at a relatively small scattering angle to avoid polarization effects. The principle of operation is rather simple and may be described as follows: the radiation emitted by the x-ray tube target is usually a polychromatic band of radiation with a high relative intensity of the characteristic radiation of the target. A crystal, cleaved on a plane of known spacing, is then placed in this beam and is adjusted in such a position that the Bragg angle for the characteristic radiation and the selected plane is established with the incident beam. Under these conditions only the characteristic radiation, say the K alpha line, satisfies the requirements of Bragg's law and is the only radiation reflected by the crystal. This reflected ray is then monochromatic except for the harmonics such as $\lambda/2$ or $\lambda/3$ which can usually be ignored or eliminated by control of the tube poten-

tial. If this beam is used to make diffraction diagrams, the resulting diagrams are clean with little of the confusing background usually found when white radiation is present. Simple monochromator designs have been published (Fankuchen, 6; Lonsdale, 7).

Various crystals have been suggested as monochromating crystals and these have been reviewed recently. (Lipson, Nelson, and Riley, 8). Fig. 1

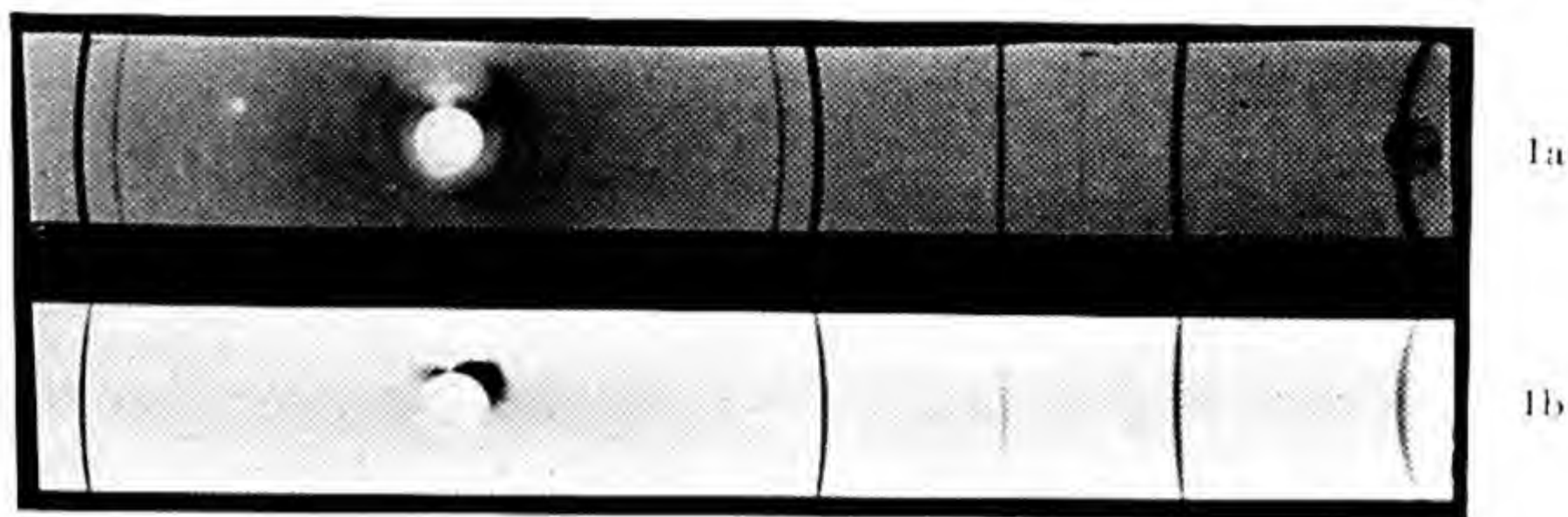


FIG. 1. Diffraction diagrams of the same iron catalyst.

1a. Taken with filtered iron radiation.

1b. Taken with iron radiation monochromatized by a penta-erythritol crystal.

shows a comparison of two diagrams of the same iron catalyst taken with iron radiation. The upper pattern, 1a, was taken with filtered iron radiation and the lower, 1b, was made using iron radiation monochromatized by a pentaerythritol crystal. The improvement is obvious and monochromatization is practically a necessity for careful study of these materials.

(b) Bent crystal or focusing monochromators for x-rays have been known for some time and have the advantage of conserving the normally divergent radiation by focusing the beam to a sharp line, and thus of permitting the use of shorter exposure times if certain geometrical conditions are fulfilled. The conditions are that the source of x-rays, the bent crystal, and the point of focus all lie on the circumference of a circle (the focusing circle). The crystal is bent into a cylinder of radius twice the radius of the focusing circle and then its inner surface is ground to the radius of the focusing circle to satisfy the focusing conditions and Bragg's law. Monochromators of this type have been adequately described. (Guinier, 2; Johansson, 9; Bozorth and Haworth, 10; DuMond and Kirkpatrick, 11; Smith, 12.)

Fig. 2 illustrates the method of achieving the focusing effect by use of a bent crystal and Fig. 3 shows one of the ways in which it was used by Guinier. Fig. 4 shows a series of diagrams obtained by Guinier with this apparatus using normal exposure times. This method not only requires

exposure times which are not longer than those normally required with filtered radiation but also yields diagrams which, due to their very low backgrounds, are far superior to any obtained with filtered radiation.

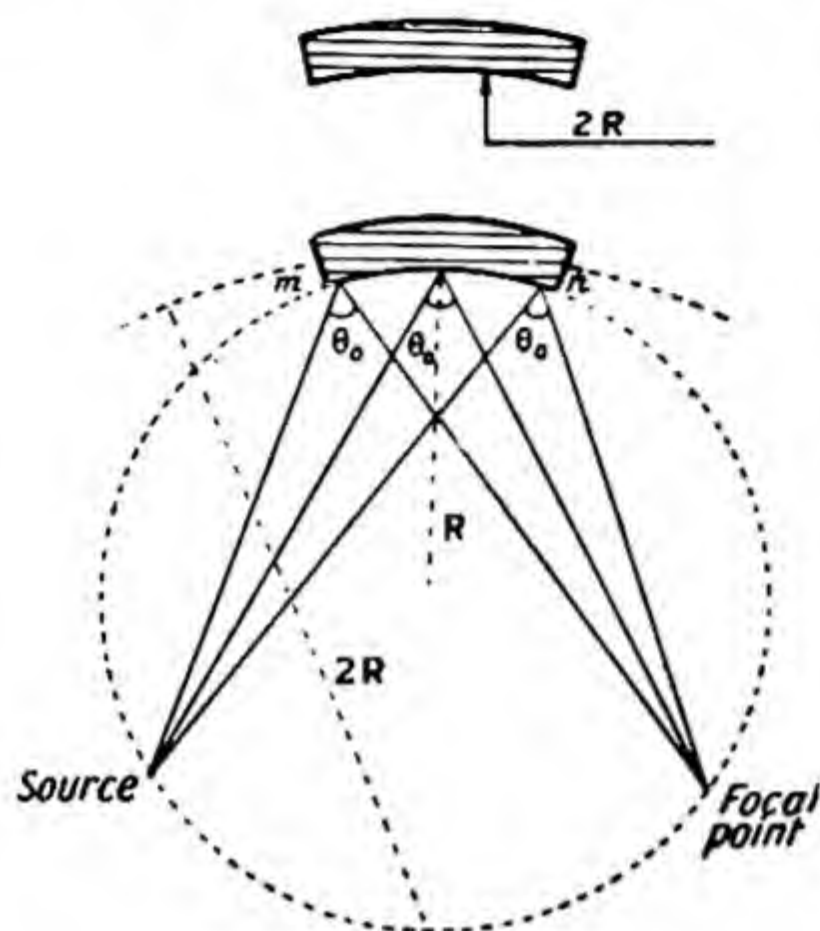


FIG. 2. Bent crystal focusing.

4. Average Crystallite Size

(a) Ordinary powder (Debye-Scherrer) diagrams can be measured so as to yield information concerning the average crystallite size of the sample. This information is obtained by measuring the widths of the diffraction lines themselves at their point of half maximum intensity. The "half breadth" can then be used to calculate the average crystallite size. Formulas for making this calculation have been published by several workers but the one most generally

used is that given by Bragg with a correction owing to Warren.

$$L = \frac{0.89\lambda}{B_c \cos \theta}$$

where

L is the crystallite diameter in Å.

λ is the wavelength of x-ray radiation in Å.

θ is the Bragg angle, i.e., one-half the angle of scatter.

B_c is the corrected width of line at half maximum intensity.

B_c as defined by Warren is given by

$$B_c = \sqrt{B_0^2 - B_e^2}$$

where

B_0 is the measured width of line in radians at half maximum intensity.

B_e is the measured width at half maximum of a well crystallized material at approximately the same scattering angle.

Strictly, this formula applies only when several stringent conditions are fulfilled. The radiation used should be monochromatic and the lines well resolved. It also assumes strain free crystals in the form of perfect cubelets all of about the same size.

It should be pointed out that two methods are currently available commercially for recording and measuring the intensities across the widths of x-ray diffraction lines. The first consists of registration on a photo-

graphic film followed by microphotometering. The second uses the x-ray spectrometer. The former method requires a relatively expensive micro-

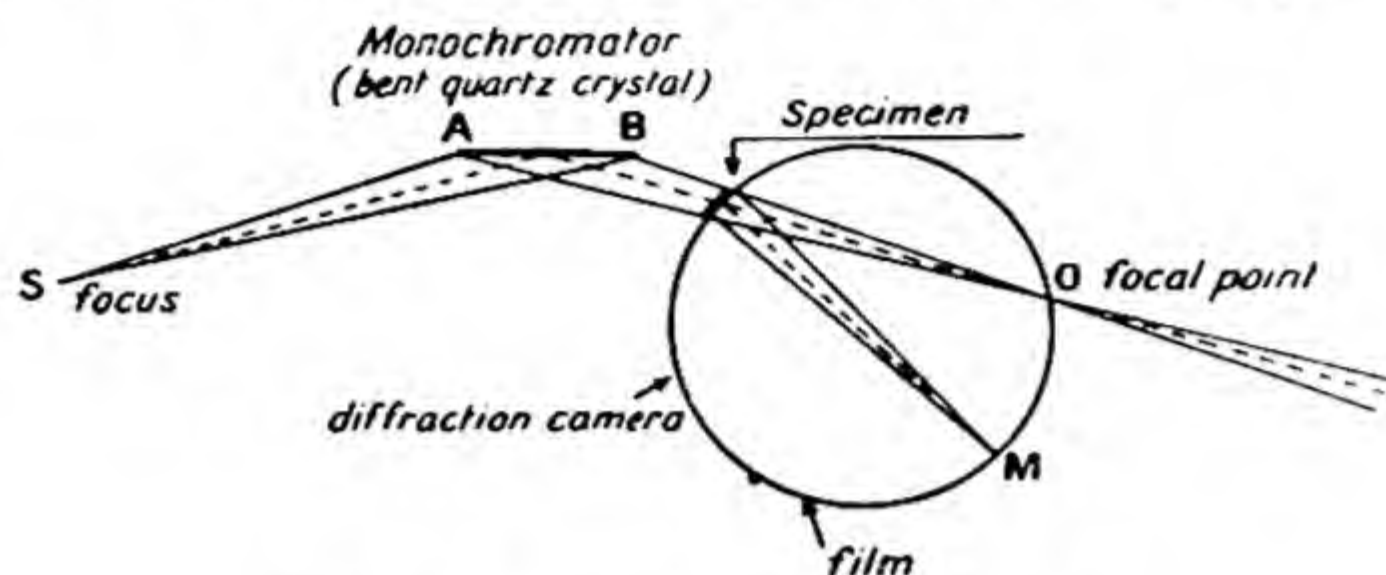


FIG. 3. Bent crystal focusing camera.

photometer and the latter usually gives abnormal line shapes due to certain features of the apparatus. In both instances, it is necessary to run as a standard a well-crystallized specimen to obtain the correction factor of the particular apparatus used. Furthermore, when a wide range of crystallite



FIG. 4. Powder patterns obtained with monochromatic $\text{CuK}\alpha$ radiation from a bent crystal.

- a Nickel foil (5 minutes)
- b NaCl
- c Aluminum alloy containing Al_2Cu

sizes is present in the solid under investigation the theory is not directly applicable.

5. Particle Size from Small Angle Scattering

The 'particle' is one continuous piece of the material regardless of the orientation of the crystallites of which it may be composed. Thus, a particle can never be smaller than one crystallite but may be composed of one or more.

As this field of x-ray scattering measurements is not as generally well known and used as some of the others, it will be more completely discussed.

a. General Theory. The phenomenon of small angle scattering, after its prediction by Debye (3), for substances having discontinuities, was observed by Guinier who made photographs of this "central blackening" using a bent crystal monochromator of the type already described. Guinier (2, 13) also published much of the theory. It has been shown (Guinier, 2, 13; Hosemann, 14; Jellinek and Fankuchen, 5; Kratky, Sekora, and Treer, 15) that for a homogenous assemblage of spherical particles of radius R , the small angle scattering of x-rays of wavelength λ can be fairly accurately given by

$$I(\theta) = CW R^3 e^{-\frac{k^2 R^2}{5}} \quad (2)$$

where

$I(\theta)$ is the intensity of scattering as a function of θ

$$k = \frac{4\pi \sin \theta}{\lambda} = \frac{4\pi \theta}{\lambda} \text{ (for small } \theta \text{)}$$

W is the mass of the scattering specimen

C is a constant for a given material

For this case, a plot of $\log I(\theta)$ against θ^2 should give a straight line whose slope will be a function of R . Thus for a preparation consisting of particles of approximately the same size (in the range ca. 50–1000 Å. diameter) a study of the small angle scattering of x-rays should permit the determination of the particle size.

The discussion to this point has assumed that particles of only one size are present, which will seldom, if ever, be the case in actual practice. When a weight distribution of sizes exists, which is given by $W(R)$, where $W(R)$ is the weight fraction of radius R , then the curve of scattered radiation as a function of theta is given by

$$I(\theta) = C \int_0^{\infty} W(R) R^3 e^{-\frac{k^2 R^2}{5}} dR$$

Now, the plot of $\log I$ against k^2 or θ^2 is no longer a straight line. In practice, the scattering curve is determined experimentally and $W(R)$ is the desired result. Various workers have shown both analytically (Bauer, 16; Roess, 17) and graphically (Jellinek, Solomon, and Fankuchen, 18; Roess and Shull, 19) that a particle size distribution can be obtained from the experimental data. While the analytic solutions would be more exact, the theory at present is still in not too good a state and has been used in cases for which the assumptions underlying the theory do obviously not apply. For these reasons it is felt that the graphical analysis is preferable and adequate at present.

b. Techniques of Measuring Small Angle Scatter. The usual small angle apparatus consists of some type of collimating system of considerable length to keep down to a minimum the divergence in the beam, sometimes

combined with crystal monochromatization. (Alternatively a bent crystal focusing monochromator can be used.) The beam is then passed through the specimen and the scattering is recorded, usually at a fairly large distance from the specimen, especially when bent crystal monochromatization is not used.

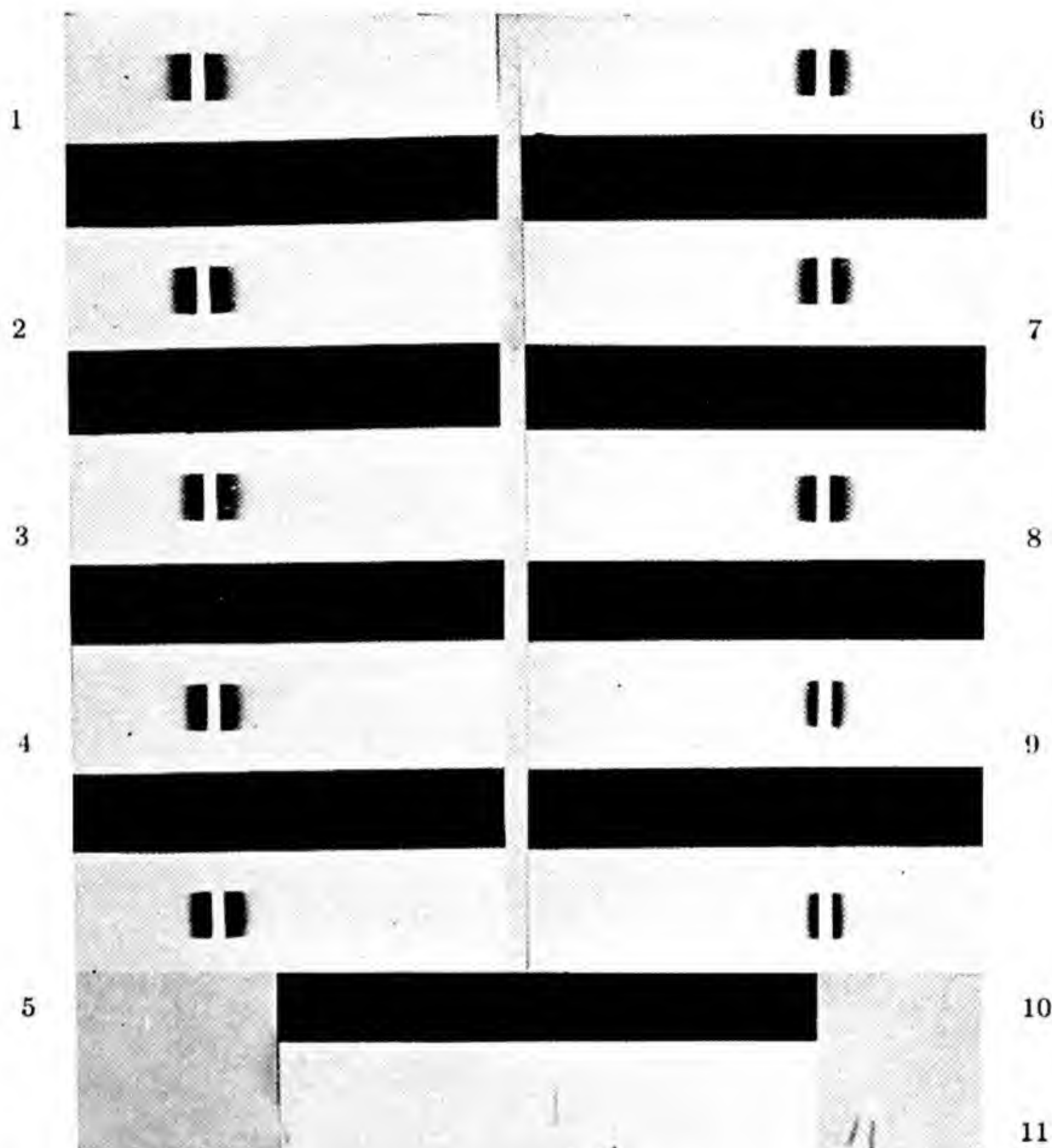


FIG. 5. Photographic record of small angle scatter showing the changes produced by heating gamma-alumina.

(1) Photographic recording requires that a cassette be provided to hold the film perpendicular to the x-ray beam. A stop, usually of lead or silver, is located a short distance in front of this cassette to catch and absorb the direct beam from the collimator to prevent it from halating the

film and thus destroying the small angle region. Fig. 5 shows a series of small angle diagrams taken at 600-mm. distance between specimen and plate, of a specimen of heated active alumina. (The larger the number in the diagram, the more severe the heating.) Filtered copper radiation was used. The change in the size of the small angle scatter can be noted, especially in the latter portion of the second column. Intensity measurements must be made over an intensity range of several thousand to one. This is a difficult task if photographic recording is used. For this reason, resort has been made to Geiger counters for recording the x-ray intensities. Fig. 6

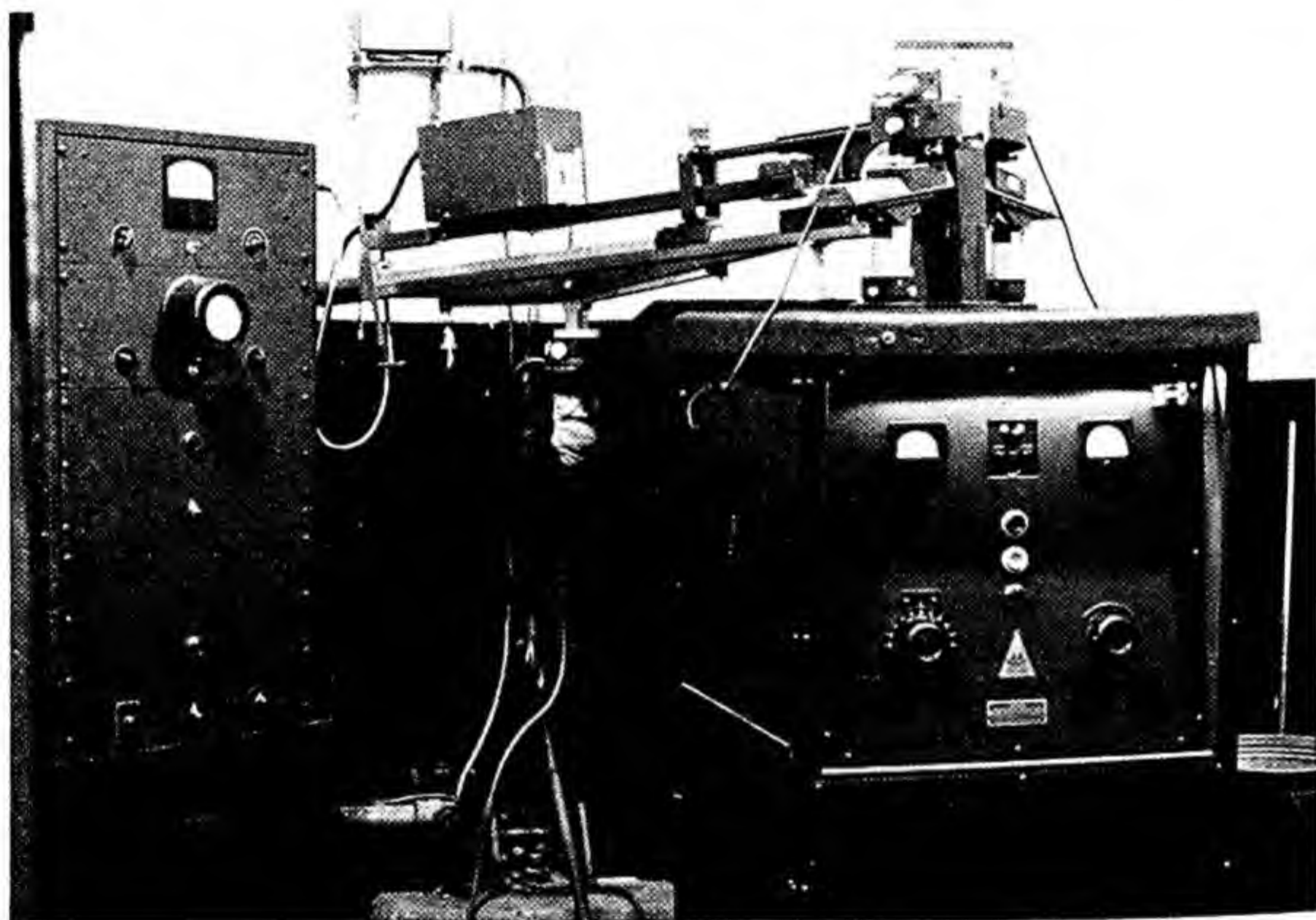


FIG. 6. Small angle scatter apparatus with Geiger counter.

shows such an apparatus (Jellinek, Solomon, and Fankuchen, 18). The scanning unit was mounted on pivots that allowed it to be rotated about the point where the x-ray beam and the specimen intersected. Measurements made with this apparatus and with the photographic apparatus are compared in Fig. 7. In this figure, the intensity scale is relative and it is only the shapes of the curves that should be compared. It can be clearly seen that the agreement is good except in the high intensity region where a deviation is expected and encountered due to the poor photographic response of the photographic film in this region. Another important advan-

tage of the Geiger counter apparatus is its higher sensitivity as compared with film. Figure 7 shows the Geiger curves out to angles where it was also possible to obtain photographic recording. Actually, the counter apparatus shown permitted reliable measurements to be made over about twice the angular range covered by the photographic method. Moreover the time required to collect the data with the Geiger counter was only about one-quarter the time required for the equivalent photographic exposure.

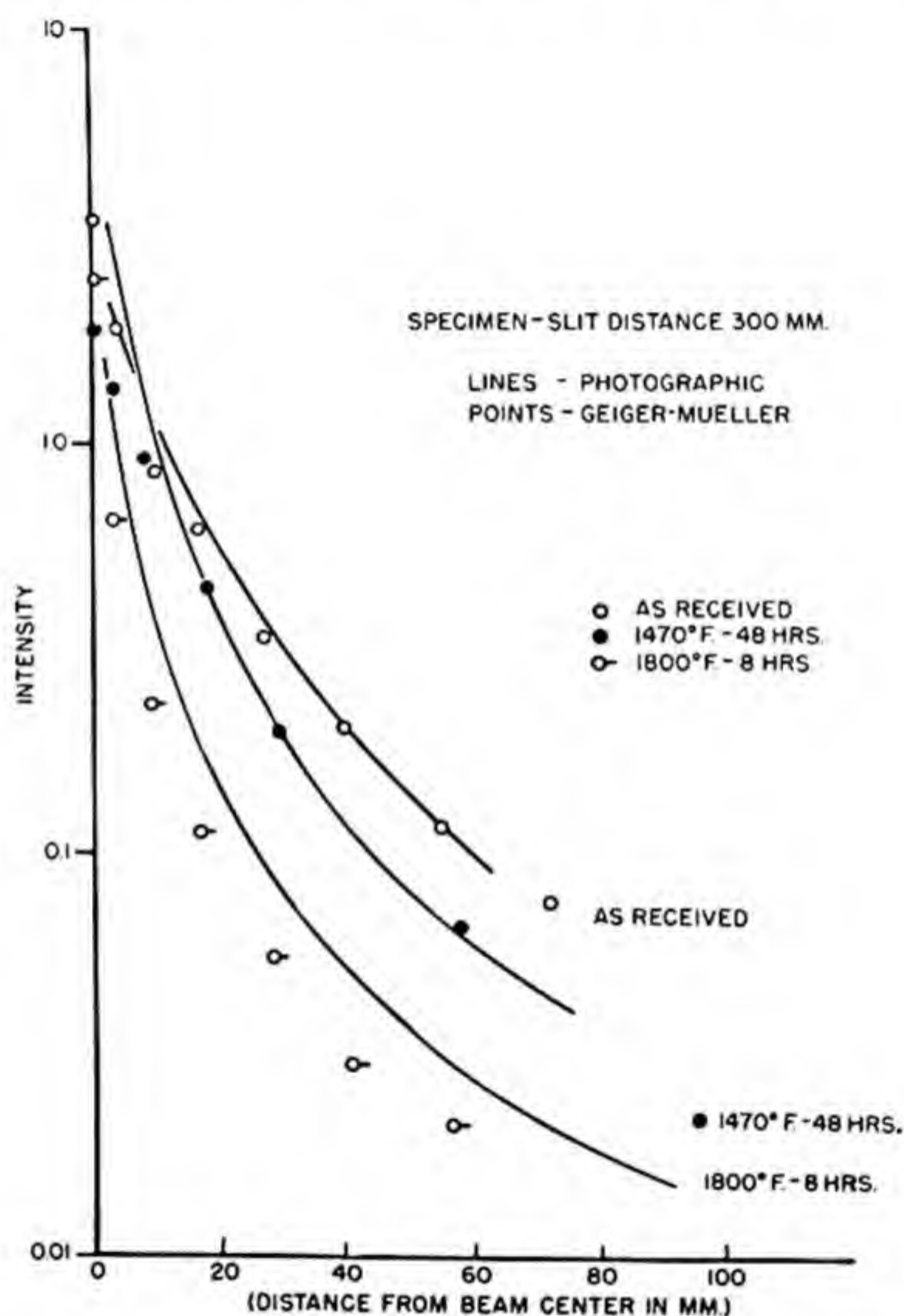


FIG. 7. Comparison of Geiger-Mueller and photographic measurement of small angle scatter of heated gamma-alumina.

Small angle scatter measurements using plane crystal monochromatized radiation and photographic recording were carried out by Shull and Roess (19) and using bent crystal focused monochromatic radiation and photographic recording by Guinier (2, 13) in the apparatus described earlier.

Small angle scatter measurements can also be made with the Philips'

x-ray spectrometer, only a few simple changes being necessary. Fig. 8 shows this apparatus. All that is needed is an extra defining slit in the x-ray beam path placed near the axis of the instrument and a modified specimen holder. The specimen is first placed between the x-ray tube and the added slit and the small angle air scatter around the main beam is measured with the beam weakened by the absorption of the specimen. The specimen is then moved to its location over the rotation axis of the instrument and the scatter is again measured. After subtracting the blank from the latter measurement, the resulting figures represent the small angle scatter of the specimen.

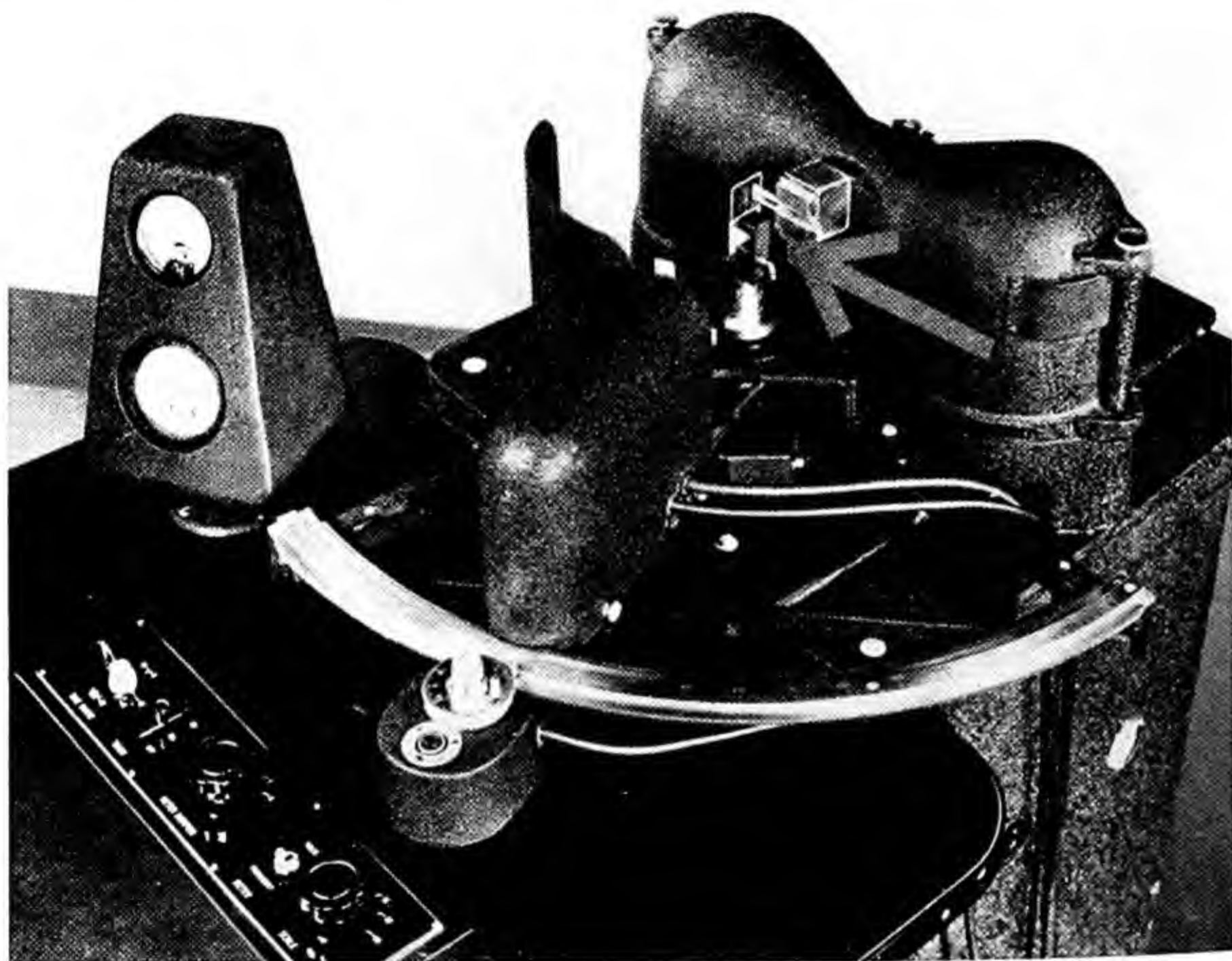


FIG. 8. X-ray spectrometer with arrow indicating position of slit to convert for small angle scatter.

Neither the film methods nor the Geiger counter method, as described above permit the measurement of the scattered radiation in the close vicinity of the main beam because of its high intensity and its halating effect on the film. The use of absorbers is a tedious task even with monochromatic radiation and film, and becomes hopeless when white radiation is

present. In many cases, however, it is rather important to know the scatter at very small angles, in fact right to zero angle, in order to make as complete an analysis as possible. The reason for this need is seen from Table I which presents the angle at which the scattering has fallen to one-half its theoretical value at zero angle for various particle sizes. It is quite obvious that larger particles require measurements close to zero angle and that for samples containing a considerable percentage of large material a significant part of scatter may be lost if the scattering at very small angles is ignored.

TABLE I

Radius in A.	Angle 2θ in minutes at which intensity of small angle scattering has fallen to half of value at zero angle
25	63.0
50	31.5
100	15.8
200	7.9
400	3.9
Computed for copper $K\alpha$ radiation	

It appears that this difficulty may be overcome by a different method (Fankuchen and Jellinek, 20; Warren, 21) of measuring small angle scattering ("Two crystal method"). Fig. 9 is a schematic drawing of such an

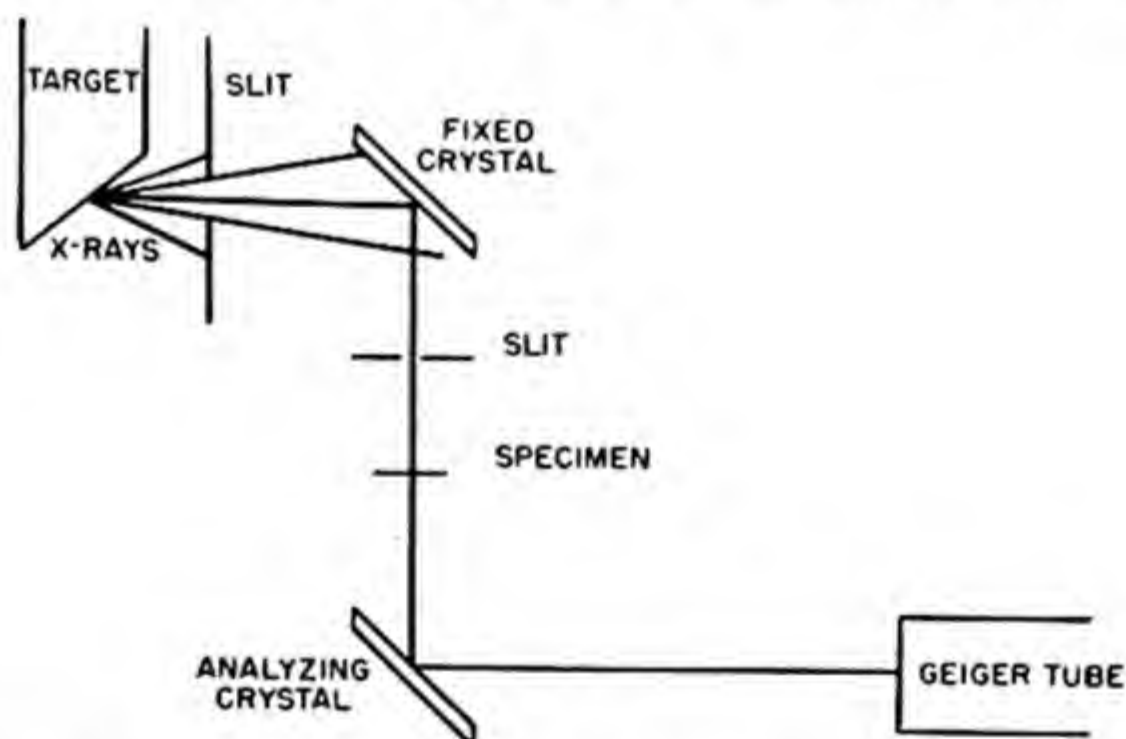


FIG. 9. Schematic representation of the two-crystal small angle apparatus showing the defining slit, fixed crystal, specimen position, analyzing crystal, Geiger tube, and optical path.

apparatus. A calcite crystal is set up as a monochromator, which because of its perfection reflects a beam of very narrow width. At a reasonable distance from this fixed monochromatizing crystal, another calcite crystal

is set up so that it can reflect the beam from the first crystal. Thus, when reflections from both crystals occur, the two reflecting crystal faces are parallel. If this second "analyzing" crystal is rotated about an axis lying in the face of the crystal at the point where the reflected beam from the first crystal hits it, the beam leaving the second crystal and falling on the Geiger tube will vary in intensity. In this manner, the angular dependence of the intensity from the first crystal can be determined. A sample can

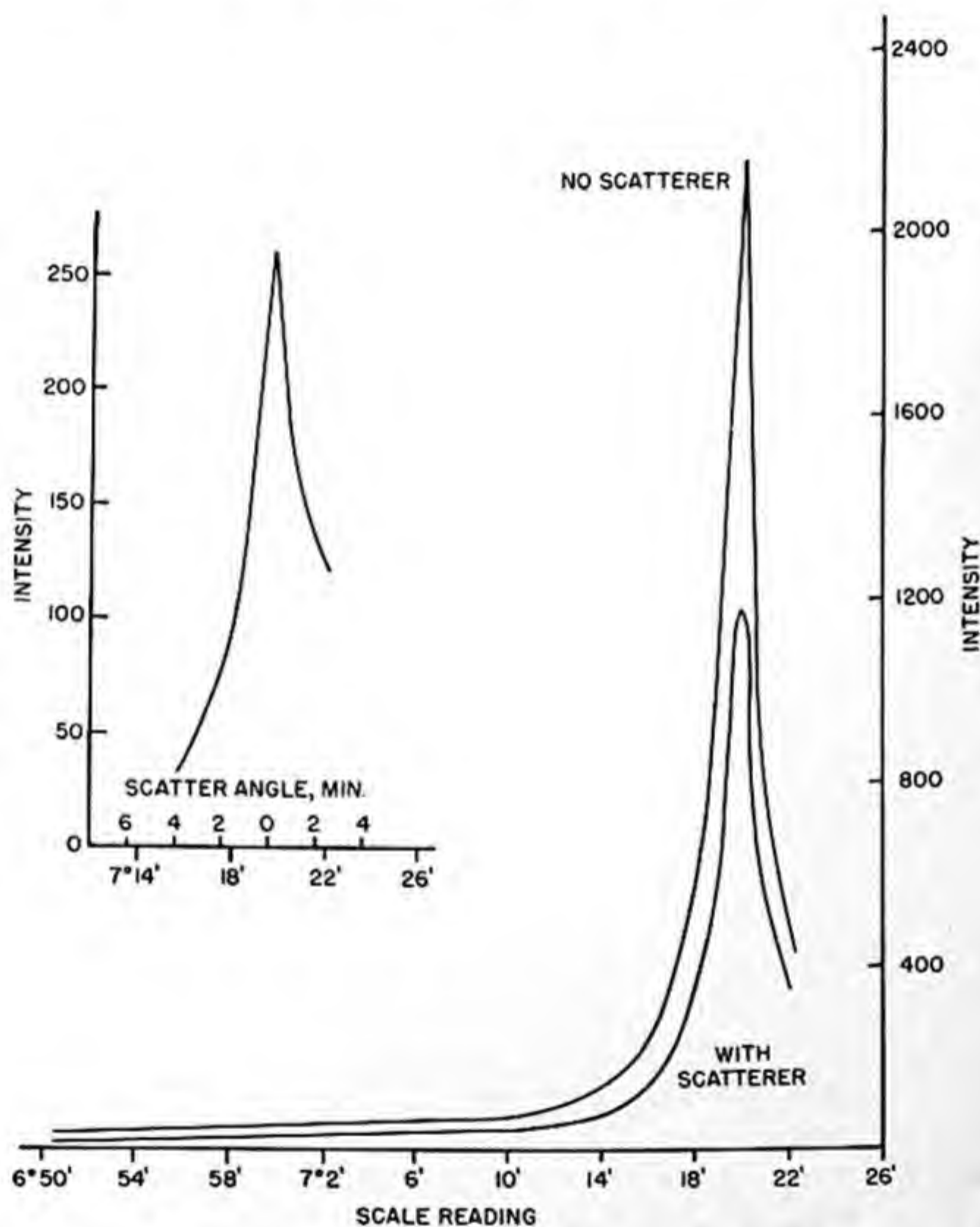


FIG. 10. Two crystal method for measuring the small angle scatter of gamma-alumina.

then be inserted between the crystals and the scattering again measured. The difference between the scattering before and after insertion of the sample represents small angle scatter of the specimen through to zero angle. A correction for air scatter must also be applied to these measurements. Because of the weakness of the doubly reflected beam, only the

scattering at very small angles can be measured in this way. Fig. 10 shows the results of such measurements on a sample of alumina gel and Fig. 11 shows a complete small angle scatter curve made by combining the results of the standard and of the two crystal methods. It is clear that in this particular instance, neglecting the very small angle scattering would have meant the loss of the information on a very large portion of the sample. On very finely divided materials, however, results indicate that a study of the neglected region would not be very important.

The other straightforward method of measuring small angle scatter is that of Guinier (2, 13), in which the focused radiation from the bent crystal is passed through the specimen. If the camera is so designed that the specimen and focus lie on the circumference of the same circle, focusing conditions also prevail for the small angle scatter and high intensities are obtained suitable for photographic or Geiger recording. Fig. 3 shows this arrangement.

The two crystal method is actually a procedure for using the double crystal spectrometer of x-ray spectroscopy for the measurement of small angle scattering. Recently Warren (21) has described an ingenious way of using the two crystal spectrometer to measure what may

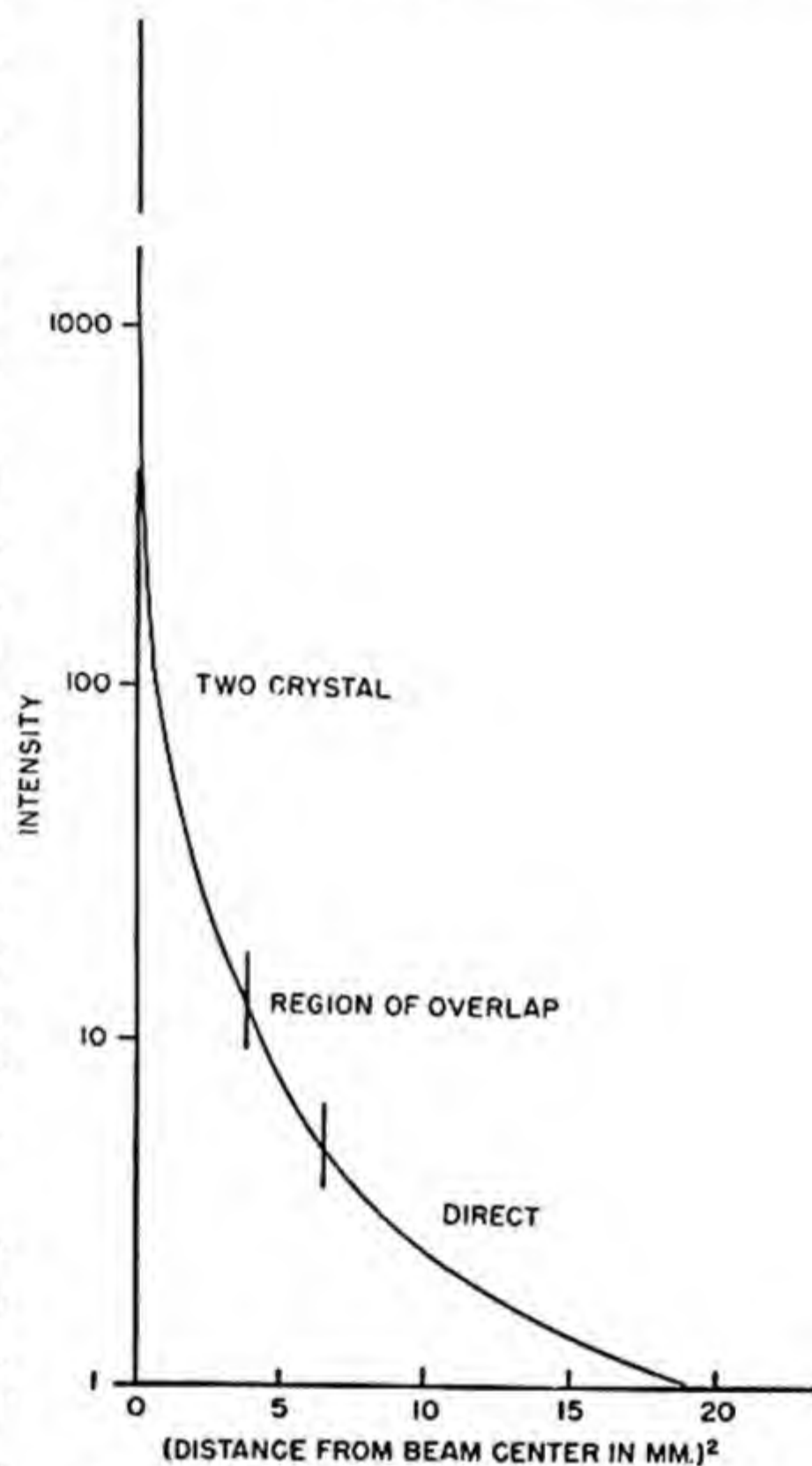


FIG. 11. Small angle scatter of alpha-alumina; combination of direct and two crystal methods of measurement.

be called total or integrated small angle scattering. The crystals are both fixed at the Bragg angles, i.e., to give maximum reflection of the characteristic radiation. Three readings are then taken. The first is made with no specimen in the beam, the second with the specimen between the two crystals and the third with the specimen in front of the Geiger counter slit (which can be quite wide). When the specimen is between the crystals, it subtracts energy from the incident beam due both to absorptive processes and to small angle scattering. The reading with the specimen in the third position will be higher because now the small angle

scattering can enter the slit and be recorded by the Geiger counter. The difference between the last two readings measures the *total* small angle scattering which can be placed on an absolute basis by using the first reading. While this method does not give the angular variation of scattering, it is, nevertheless, very simple and rapid. It would appear that a standardized "Warren" number may prove to be a useful way of characterizing many finely divided materials.

IV. LATTICE CONSTANTS

Lattice constants and variations of these constants have occasionally been discussed as being related to the specific activities of certain catalysts. The poor x-ray diagrams usually obtained with high surface materials do not lend themselves to such determinations, particularly if it is considered that the lattice constants in the uppermost surface layers of the catalyst would have to be measured in order to give information on the catalytic properties. The dimensions of a lattice of a given crystal are usually a function of the temperature at which the crystal is held. However, if other elements or compounds can go into solid solution in this crystal, changes in the lattice may occur.

There are three major types of solid solution:

1. Substitutional solid solutions are characterized by a replacement of the atoms of substance A by those of B in all proportions for materials forming continuous solid solutions or in limited amounts for those giving limited solid solutions. This replacement of substance A by B may be completely random and is designated "disorder." By careful annealing, these disordered materials may sometimes be converted to an ordered structure where each type of atom occupies a specific position in the structure. This latter effect forms a "superlattice." Solutions of this type are regarded as favorable possibilities if the radii of the atoms replacing each other do not differ by more than 15%.

2. Interstitial solutions are characterized by atoms of smaller atomic size fitting into the interstices between the larger atoms of the structure of another solid. The iron-carbon system is an example; there the carbon atoms fill the spaces between the iron atoms.

3. Subtractive solutions are formed when the solute appears to extend the solvent so that not only does replacement take place but defects appear due to the absence of a certain proportion of the solvent atoms from their expected positions.

X-ray diffraction provides a very sensitive tool for studying these effects, provided the changes concern the entire solid phase, and not merely one or a few atomic surface layers. This latter phenomenon, sometimes assumed for the explanation of catalytic activities, is not detectable

by the x-ray methods so far developed. Although the change in lattice dimension is usually relatively small, being less than 1% in most cases, the form of Bragg's law allows very accurate measurements to be made at certain angles. If Bragg's law is differentiated and the terms combined the result is $\frac{\partial \theta}{\partial d} = -\frac{1}{d} \tan \theta$. In the vicinity of $\theta = 90^\circ$, small changes in the interplanar spacing d , due to lattice changes, cause large changes in θ . As θ is measured on the film, highly accurate measurements of d , and consequently the lattice parameter, are possible if the reflections can be measured at sufficiently great angles.

PART II. EXAMPLES OF APPLICATIONS

I. IDENTIFICATION

A few chosen illustrations of the utility of identification studies in certain fields of catalysis will be discussed in some detail.

Various mixtures of barium carbonate and ferric oxide (Erchak and Ward, 22; Erchak, Fankuchen, and Ward, 23) were mechanically mixed and were subjected to heat treatment at temperatures ranging between 500 and 1000° C. The problem was then twofold; namely, to identify the reaction products and to determine the catalytic activity of the products, and if possible to relate such activity to the reaction products.

As all the compounds contained iron, filtered iron radiation was used to minimize fluorescence, and thin pyrex fibers coated with the specimen were used for the photographic recording of the x-ray diagrams while specimens mixed with vaseline on microscope slides were used for all measurements on the x-ray Geiger counter spectrometer. All diagrams were measured as to the relative intensities of the lines. One unique line of each compound, not interfered with by lines of any other compound formed, was carefully measured for intensity determination after careful scanning, by counts, on the spectrometer. Thus, if intensity of the chosen line was plotted for a given temperature as a function of composition, an extrapolation to zero intensity would give the composition at which that phase disappeared.

Over one hundred preparations of the two initial constituents were made and studied. Fig. 12 shows typical powder diagrams obtained in this study along with the compounds identified. The changes occurring are clearly indicated on these diagrams.

Similarly, curves were plotted of the intensity of the chosen line as a function of temperature for a given composition. Obviously conclusions as to thermal stability, etc., can be arrived at from such curves.

To follow the changes occurring in these experiments, the use of contour

diagrams was introduced. In these, a graph was constructed with temperature as the ordinate and composition as the abscissa. Then, for each phase, the intensity of the chosen line for each pair of temperature-composition

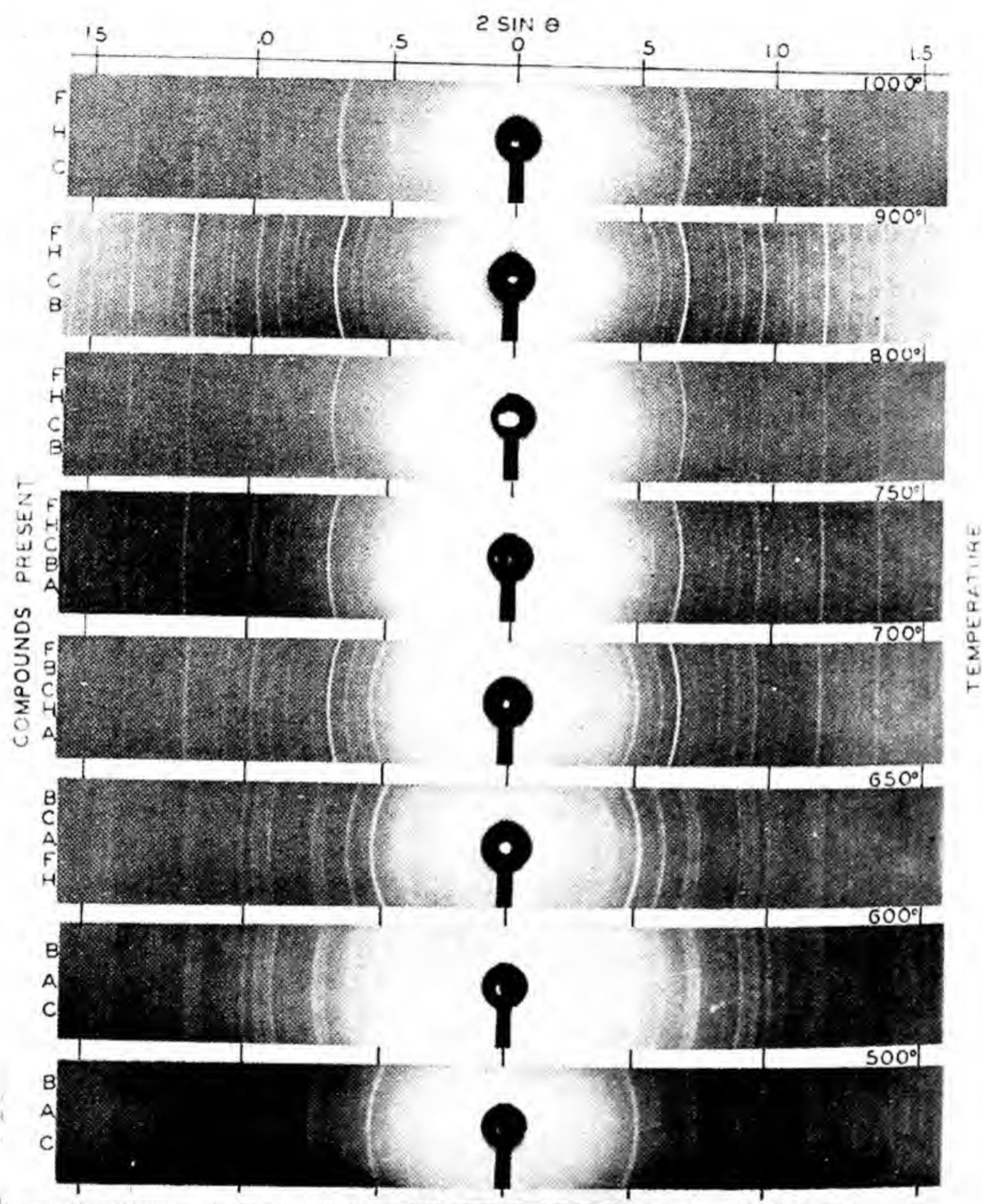


FIG. 12. X-ray diffraction patterns of products obtained at various temperatures from barium carbonate-ferrie oxide mixtures containing 70% ferrie oxide: A, ferrie oxide; B, barium carbonate; C, barium oxide; D, $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$; E, $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$; F, $\text{Ba}_3\text{Fe}_8\text{O}_{21}$; H, extra lines in pattern of F.

values was plotted and points of equal intensity were connected. Such a contour diagram is shown in Fig. 13. This diagram shows that most barium oxide was present in the samples which initially contained between 35 and

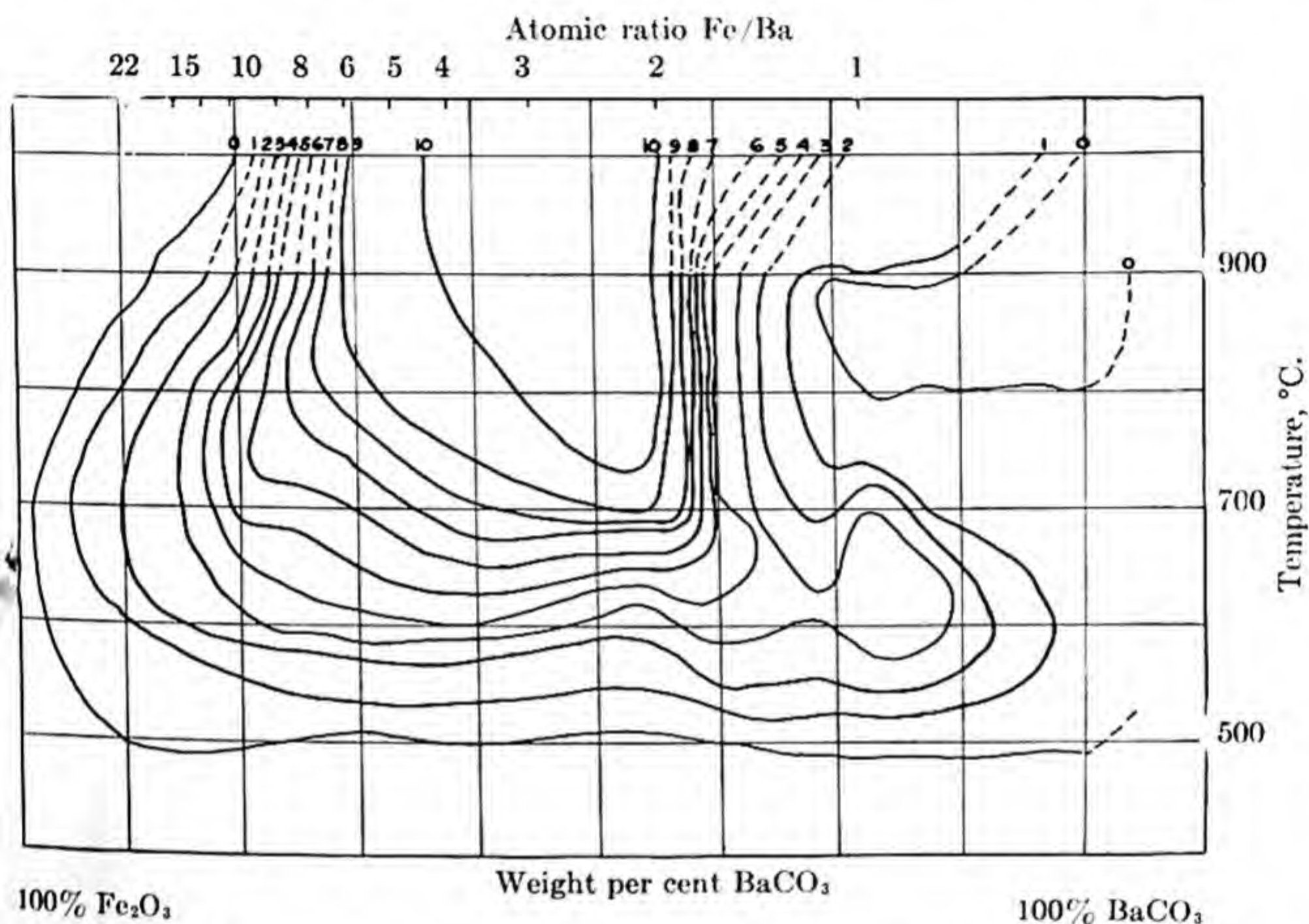


FIG. 13. Variation in concentration of barium oxide with composition of mixture and temperature of preparation.

55% BaCO₃ and after heat treatments of the samples at temperatures above 725° C. It was even possible by this method to locate completely closed regions indicating the formation of compounds of limited thermal stability. Fig. 14 shows such a situation for the compound BaO·2 Fe₂O₃. In order to complete the identification of compounds formed in this reaction, Fig. 15, giving the regions of formation of compounds E and F, is shown. These compounds have been tentatively identified as BaO·6 Fe₂O₃ and Ba₈Fe₈O₂₁, by analogy with other known compounds.

Thus by the use of the contour diagrams, the compositions of all the specimens were determined and this justified an attempt to correlate the catalytic activities of these same mixtures with their constitution.

It is frequently the case that substances prepared by the interaction of solids in the absence of fluxing materials are in a finely divided state, provided that the temperature of preparation is well below the melting points

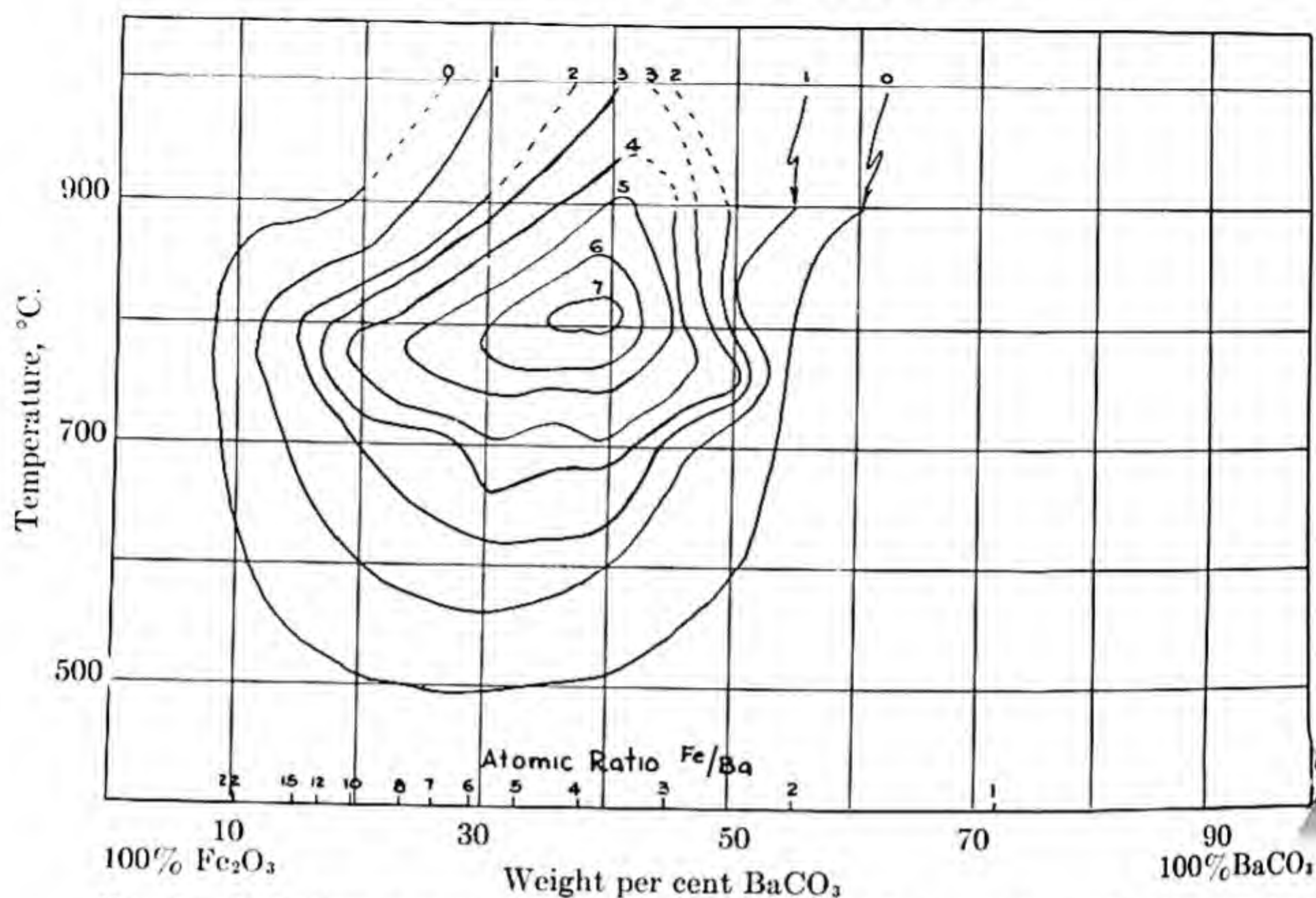


FIG. 14. Variation in concentration of $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$ with composition of mixture and temperature of preparation.

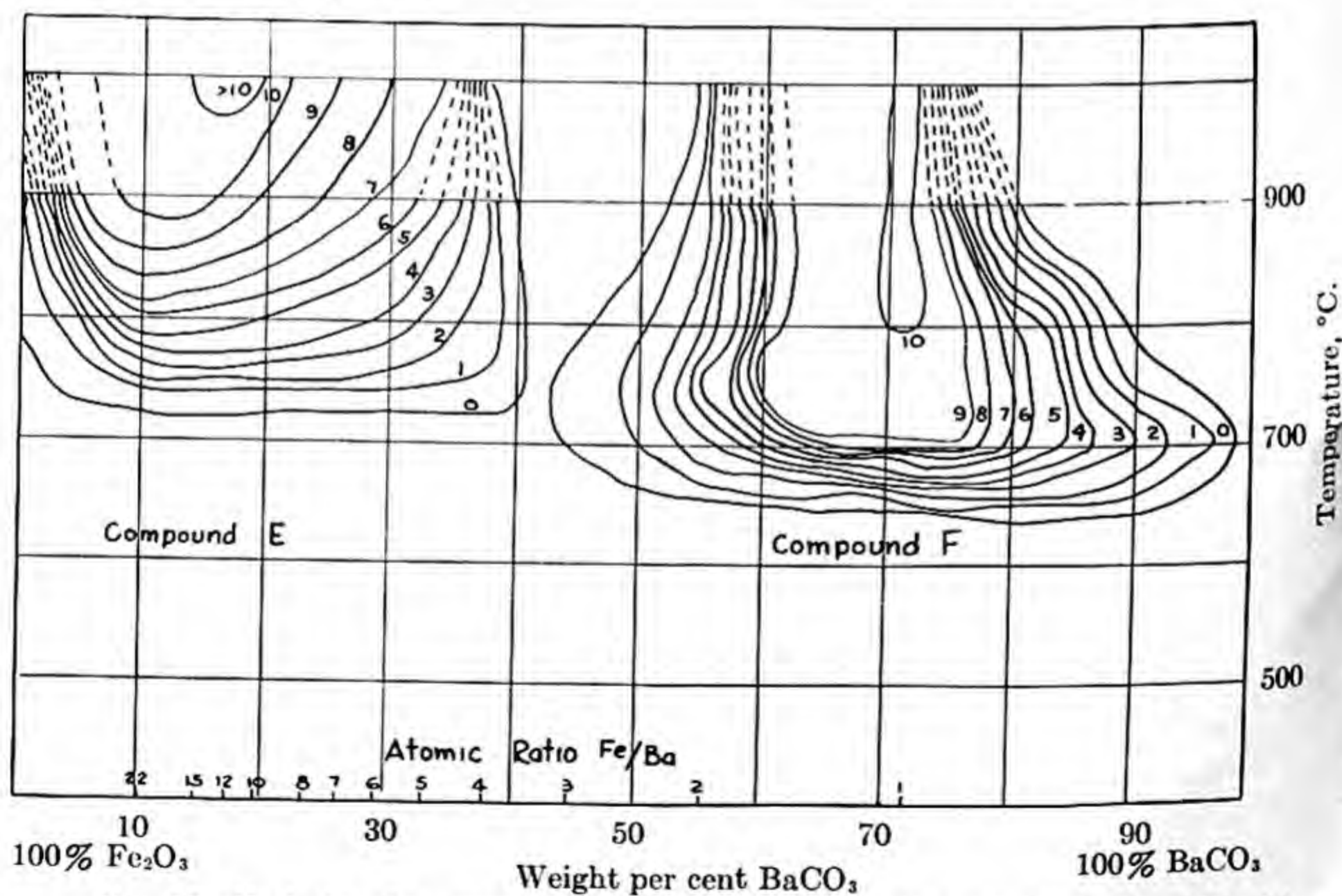


FIG. 15. Variation in concentration of $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ (E) and $\text{Ba}_3\text{Fe}_3\text{O}_{21}$ (F) with composition of mixture and temperature of preparation.

of any of the reactants, or products, or their mixtures. In the finely divided form, such materials are as a rule in a very suitable physical condition to exhibit catalytic properties. The particular reaction studied for these catalysts was the catalysis of the oxidation of carbon monoxide. Typical time-conversion curves for this reaction are shown in Fig. 16 for three of

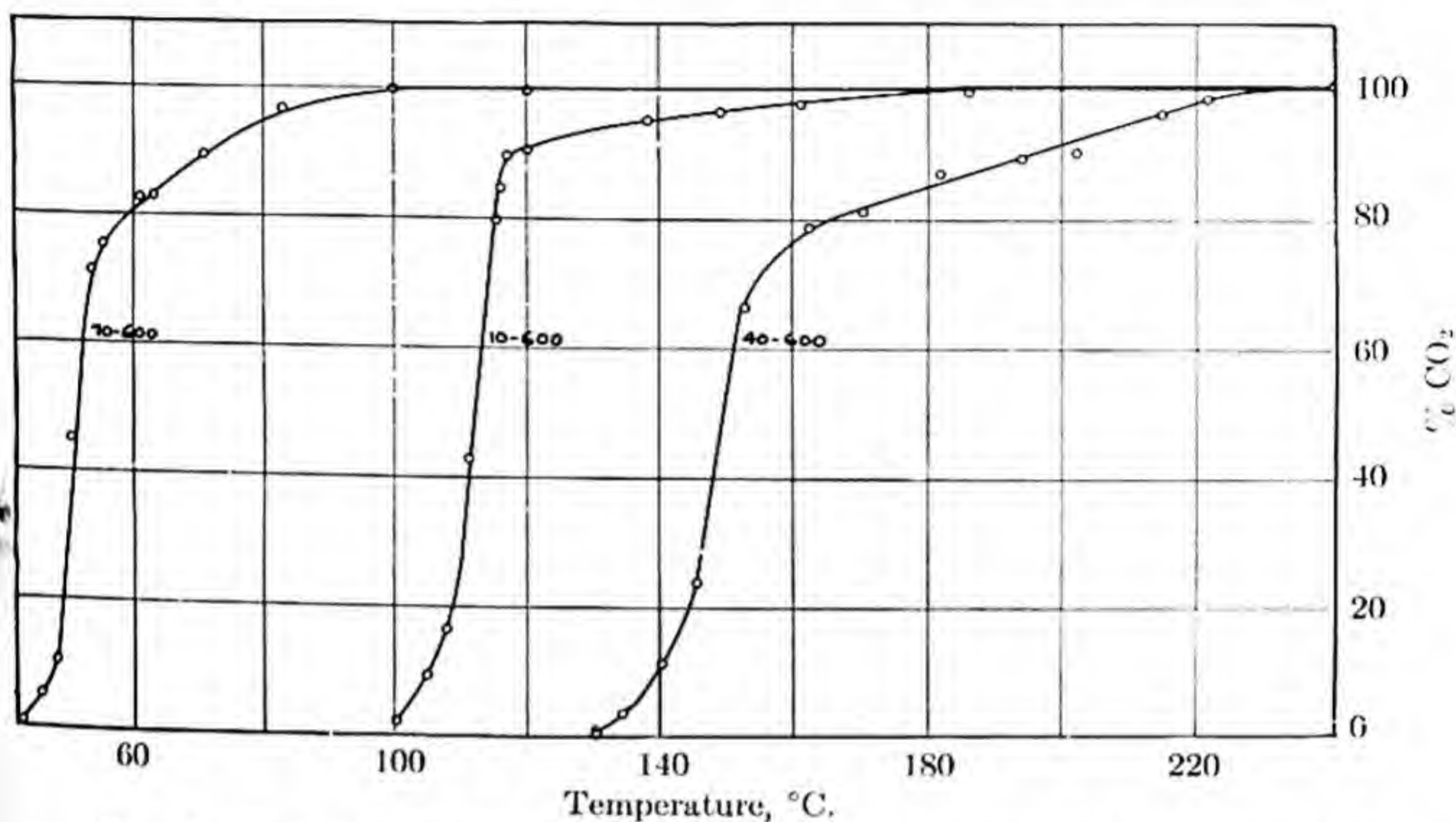


FIG. 16. Catalytic activity of several catalysts as a function of temperature in the reaction $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$.

the catalysts prepared at 600° C. and it is clear from this diagram that the catalyst made from 70% BaCO_3 is more active than that made with either 10 or 40%, because higher temperatures were necessary to attain the same conversions with the latter two as with the first mentioned.

For purposes of direct comparison, the temperature at which the catalyst gave 10% conversion was chosen as the reference point because the slopes of the curves at this point were most favorable. The 90% point gave very similar results with a few minor exceptions. For the poorer catalysts, this temperature was about 240° C., while the most active catalysts gave this conversion at -40° C. Numbers of from 1 to 15 were assigned to cover this range in 10° steps. Thus, 1 represented 240°, 2, 220°, etc. In this way, the more active catalysts were assigned the higher numbers.

To correlate the catalytic properties of the samples with their preparative temperatures and also with the results of the x-ray analysis, it was found rather convenient to construct another contour diagram. The result of this construction is shown in Fig. 17. This diagram has the composition of the starting mixture used in preparing the catalyst as abscissa and the

temperature of the heat treatment employed for the catalyst preparation as the ordinate. The numbers representing the activity of the individual samples were placed at the appropriate positions and then all similar numbers were connected in such a manner that no lines intersected. Inspection of this figure reveals that there exist certain regions of maximum activity.

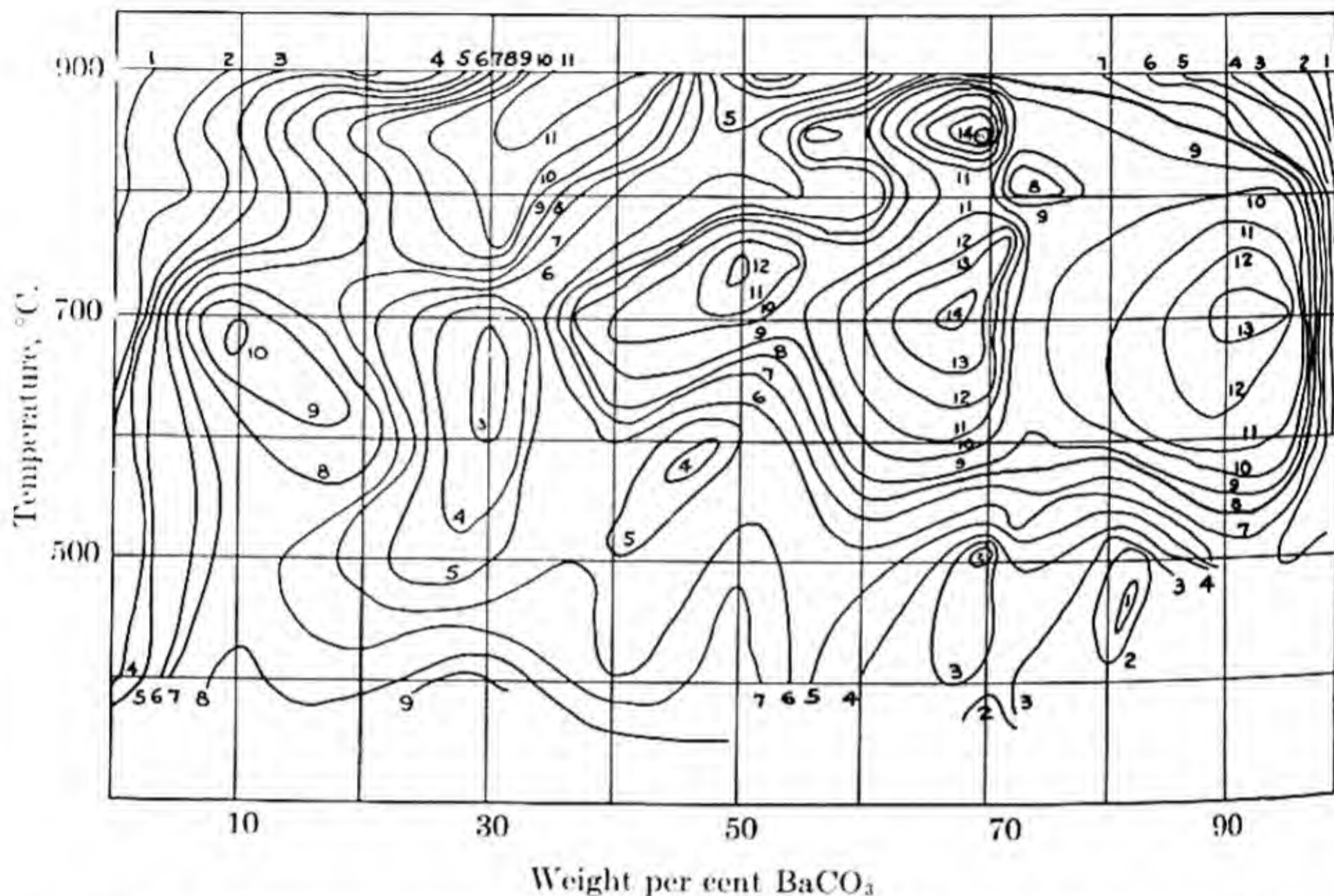


FIG. 17. Catalytic activity contour diagram showing the dependence of activity upon composition of mixture and temperature of preparation.

In the order of decreasing activity, they are 70-850, 70-700, 90-700, 50-750, etc., and there are regions where the activity falls to a minimum; for example, 30-650, 45-600, 70-500, etc. The first number refers to the percentage of BaCO₃ in the initial mixture, the second number to the temperature in degrees C. to which the mixture was heated. The active and inactive compositions could be looked up on the x-ray contour diagrams shown earlier but a far more convenient method consists in merely plotting the x-ray determined contours and the activity contours to the same scale on transparent paper and superimposing them to determine the active phases. As an example of the results obtainable, the catalysts obtained from starting mixtures with 70% BaCO₃ will be discussed in more detail.

The rapid rise in activity of these catalysts to 14 for catalyst preparation temperatures between 500 and 700° C. is followed by a decrease to 11

for a catalyst prepared at 800° C. and by a further increase to 15 for a catalyst made at 850° C. and a subsequent decrease to 8 for the catalyst made at 900° C. These catalysts were prepared from mixtures which gave the maximum amount of formation of $\text{Ba}_8\text{Fe}_8\text{O}_{21}$. No evidence of the existence of this compound was found below 650° C. A possible conclusion to draw from these observations is that the observed activity was due to this compound in small quantities or in a poorly crystallized state. As more is formed, an increase in activity is observed. Some of the variations may be attributed to the fact that this initial composition is just at the point of maximum formation of $\text{Ba}_8\text{Fe}_8\text{O}_{21}$ and, in a region of rapid change, small inconsistencies may be expected. In this manner, all the various portions of the constitution diagram can be, at least tentatively, interpreted and related to the catalytic properties of the solid phase for the CO oxidation.

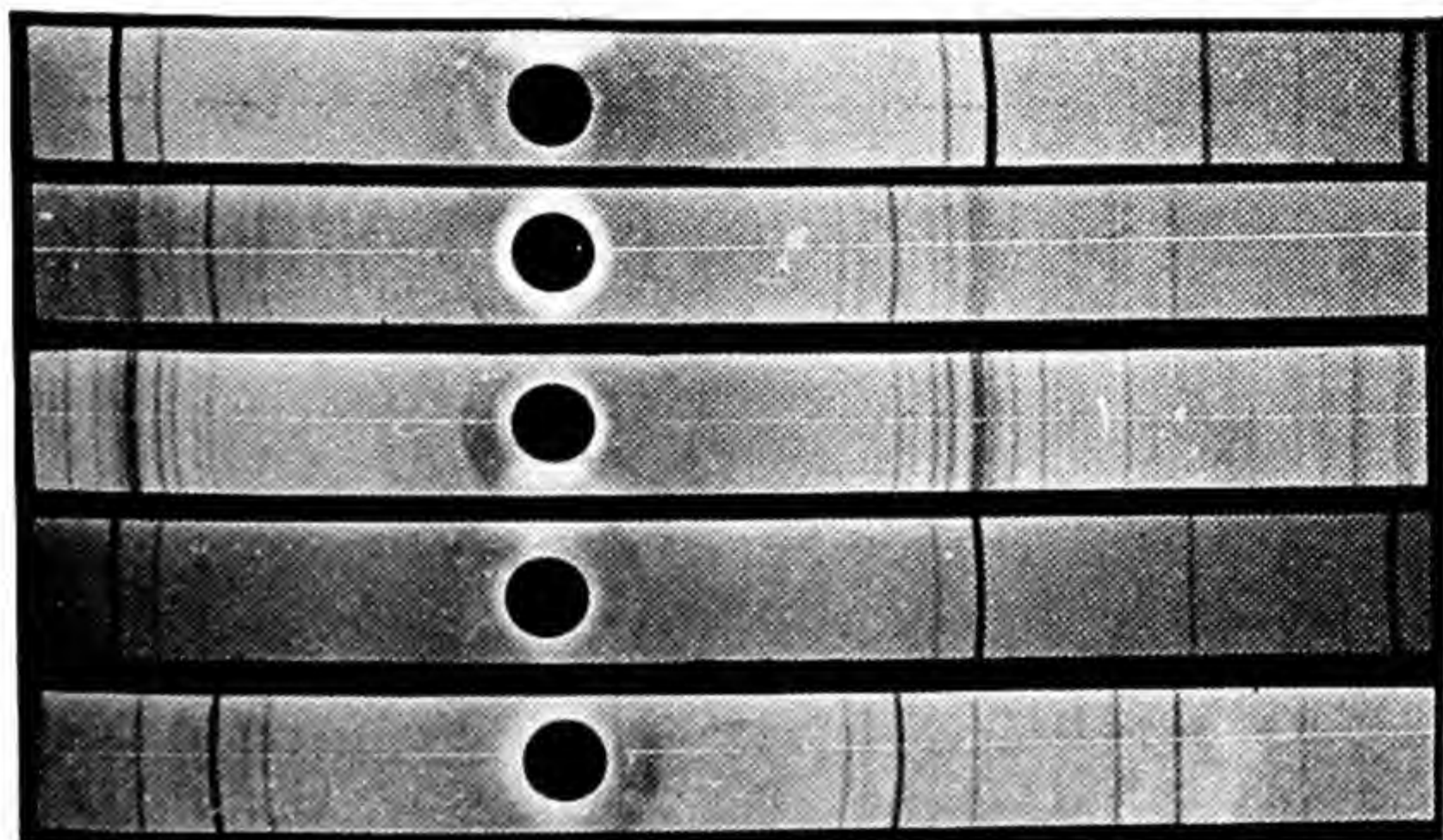


FIG. 18. Debye-Scherrer diagrams of iron Fischer-Tropsch catalysts; reduced fresh catalyst, used catalyst, used catalyst, pure iron, pure magnetite.

The Fischer-Tropsch Synthesis, i.e., the catalytic reduction of carbon monoxide by hydrogen to liquid, gaseous, and solid hydrocarbons and oxygenated organic compounds, has recently been reported to operate efficiently under superatmospheric pressure, with catalysts which contain iron as their basic component. More recently catalysts of this type are being used in a very fine dispersion which permits one to operate with them in a "fluid bed."

Such a catalyst usually consists, before the start of the synthesis reac-

tion, of magnetite, Fe_3O_4 , with a very large crystallite size. This large size of the crystallites is evidenced by the very spotty character of the powder diffraction diagrams. If the catalyst is reduced at temperatures of, say, 1500°F . in hydrogen, the product yields a diagram of metallic iron in a sufficiently finely divided form to yield smooth diffraction rings. Such a pattern is shown in the uppermost diagram of Fig. 18. As a comparison, a standard pattern of iron is shown as the next to the bottom pattern. The precise agreement in the pattern of the lines is unmistakable. After some use of the catalyst in the synthesis reaction, a sample can be withdrawn while the catalyst is still at a high level of activity and an x-ray diagram is made of this sample. (See the second diagram of Fig. 18.) It is obvious that the metallic iron has nearly all vanished and has been replaced almost entirely by magnetite. As a comparison, the final diagram of Fig. 18 shows the standard pattern of magnetite. A sample was also obtained of a catalyst which had been operated for a longer time but was still at a higher level of activity. Its diagram is the middle one in Fig. 18 and shows that the magnetite has been converted by a phase change to some other compound. While the standard pattern of this material is not included in the figure, its identity has been established as a low temperature carbide of iron, probably Fe_2C . On heating, this compound can be changed to Fe_3C , cementite. The continuous activity of the catalyst through these changes in structure is puzzling. Perhaps one should not speak of one single "Fischer-Tropsch catalyst"?

After some operation in the synthesis reaction, it occasionally becomes desirable to treat the catalyst at an elevated temperature with hydrogen in order to remove some of the waxy compounds adhering to it. Before the hydrogen treatment (provided no high pressure runs with the catalyst had been made), the catalyst is mainly magnetite, plus a little iron, and perhaps a trace of carbide. X-ray studies show that the hydrogen treatment converts the catalyst back to iron.

In a few apparently completely random Fischer-Tropsch catalysts, rather large distortions of the iron and magnetite lattices were noted. This may be due to solid solution of a variety of components.

II. CRYSTALLITES AND PARTICLES

Because of the close connection between these two phases of x-ray study, especially in the work discussed here, they will be considered together. (Biscoe and Warren, 24; Jellinek and Fankuchen, 5; Roess and Shull, 19.)

Activated alumina purchased from the Aluminum Ore Company was given a treatment with dilute hydrochloric acid to lower the sodium oxide

content from about 0.5% to less than 0.1%. This alumina, designated "low soda alumina," was then given a series of heat treatments of increasing severity. The first studies on this alumina were of a simple exploratory nature to determine what changes in diffraction effects, if any, could be detected with changes in catalyst activity. A part of this study was carried out on the alumina base. In further studies, it developed that the presence of molybdenum trioxide acted as an accelerator to the changes that occurred in the pure alumina. In other words, addition of the molybdena brought about a certain change in the alumina at a temperature which was 100° C. or more lower than the temperature at which a similar change took place in the alumina base.

Fig. 19 shows the powder diagrams of the low soda alumina that had been given the indicated heat treatments. The original sample received from the Aluminum Ore Company gave the diagram shown at the top of this figure and was easily identified as gamma-alumina. As this material was heated to higher and higher temperatures, not only did the lines in the diagrams sharpen, as can clearly be seen, but the number of diffraction rings increased. For several reasons, this seemed to indicate not the formation of any new form of alumina, but rather a development and perfection of the original structure. In the more highly heated samples, the presence of corundum or alpha-alumina can be detected by comparing the corresponding diagrams with the final pattern, which is that of alpha-alumina. That changes in particle size also occurred was indicated by the photographic small angle scatter diagrams (Fig. 5).

These basic changes of growth of crystallites and particles, and of development of the structure of the alumina base can be shown to have rather important correlations with the surface areas of the catalysts and their activities in hydroforming. One of the rather important technical problems concerning these catalysts was the prolonging of their useful life. It was found that high temperature heat treatment of hydroforming catalysts represents an accelerated test by resulting in the same changes as occur at much lower temperatures over extended periods of time in actual field service. Therefore, in studying new base materials for stability, it was a customary procedure to heat them to a given test temperature, check their activity, heat treat them more severely and continue until a temperature was attained which caused a drop in activity. This was a costly and time-consuming process.

After the advent of the x-ray techniques, a shorter test method was developed involving heat treatments of small samples, followed, instead of the usual activity test, by an examination of the powder x-ray diagrams. This permits an easy and fast detection of any deterioration of the catalyst properties by overheating because of the very marked change in the x-ray

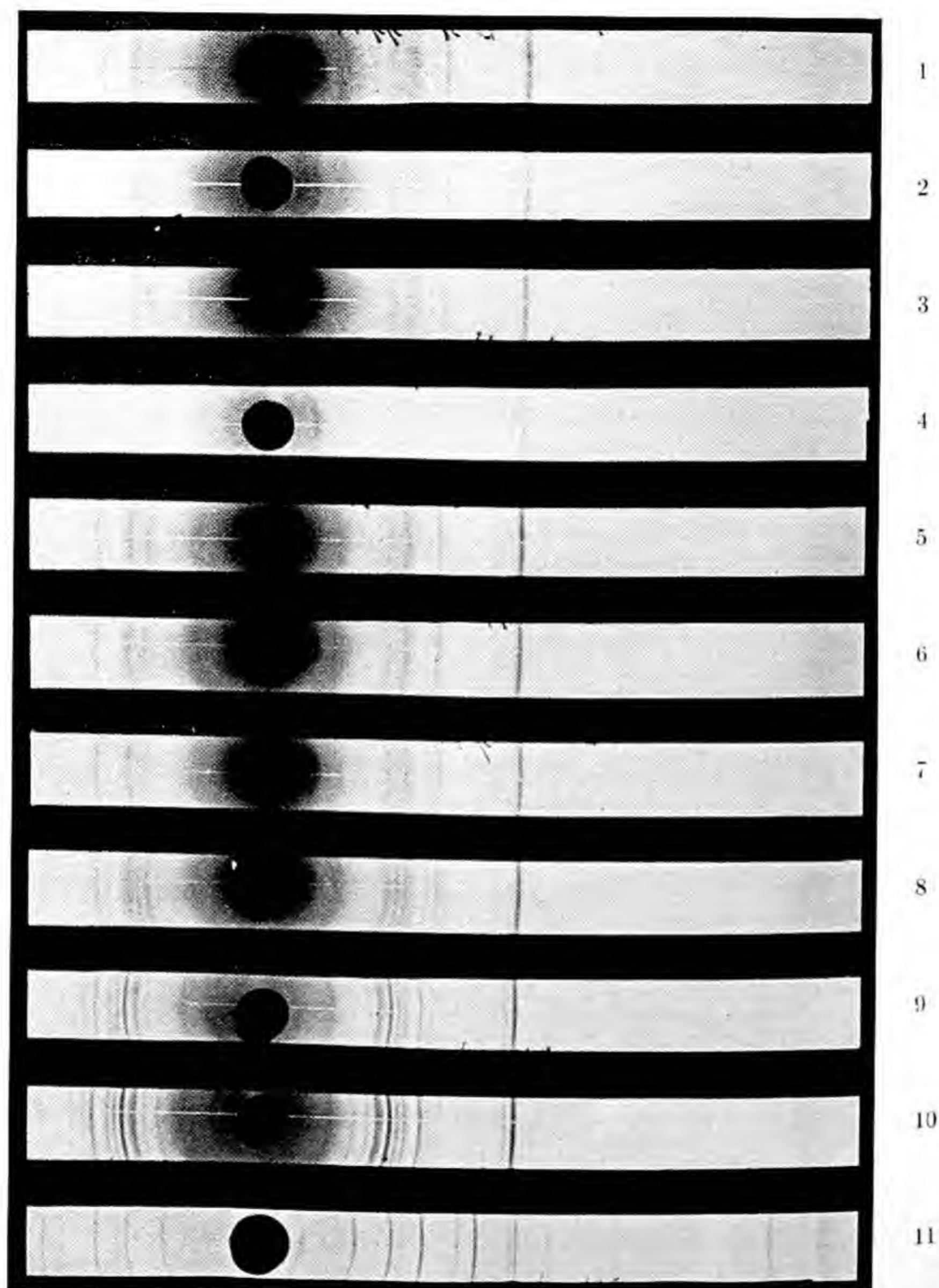


FIG. 19. Debye-Scherrer diagrams showing the effect of increasingly severe heat treatment of low soda gamma-alumina.

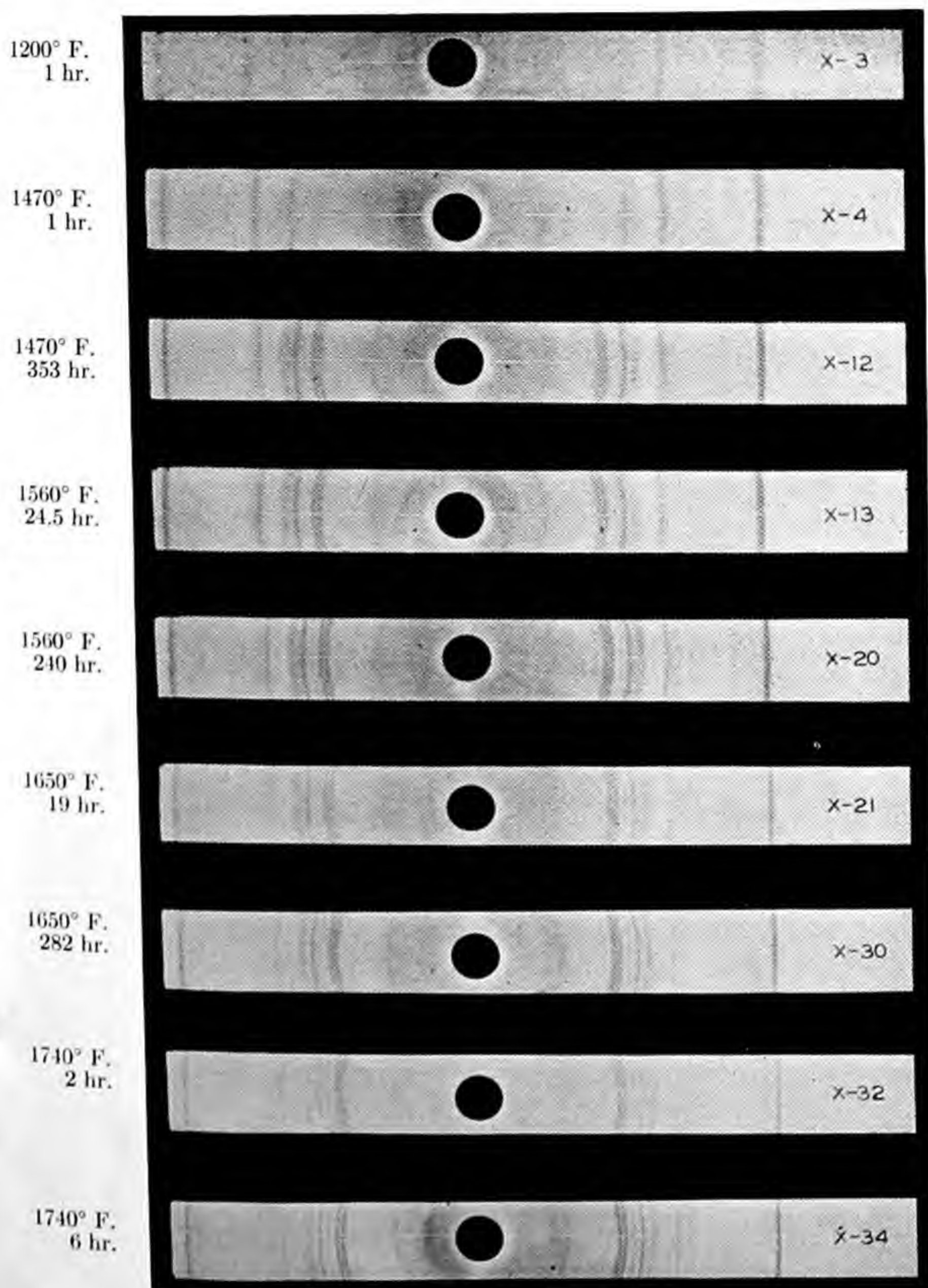


FIG. 20. Debye-Scherrer diagrams of heated alumina gel.

patterns. If the catalysts themselves had behaved as did the alumina and had shown gradual changes, the task might have been more difficult and

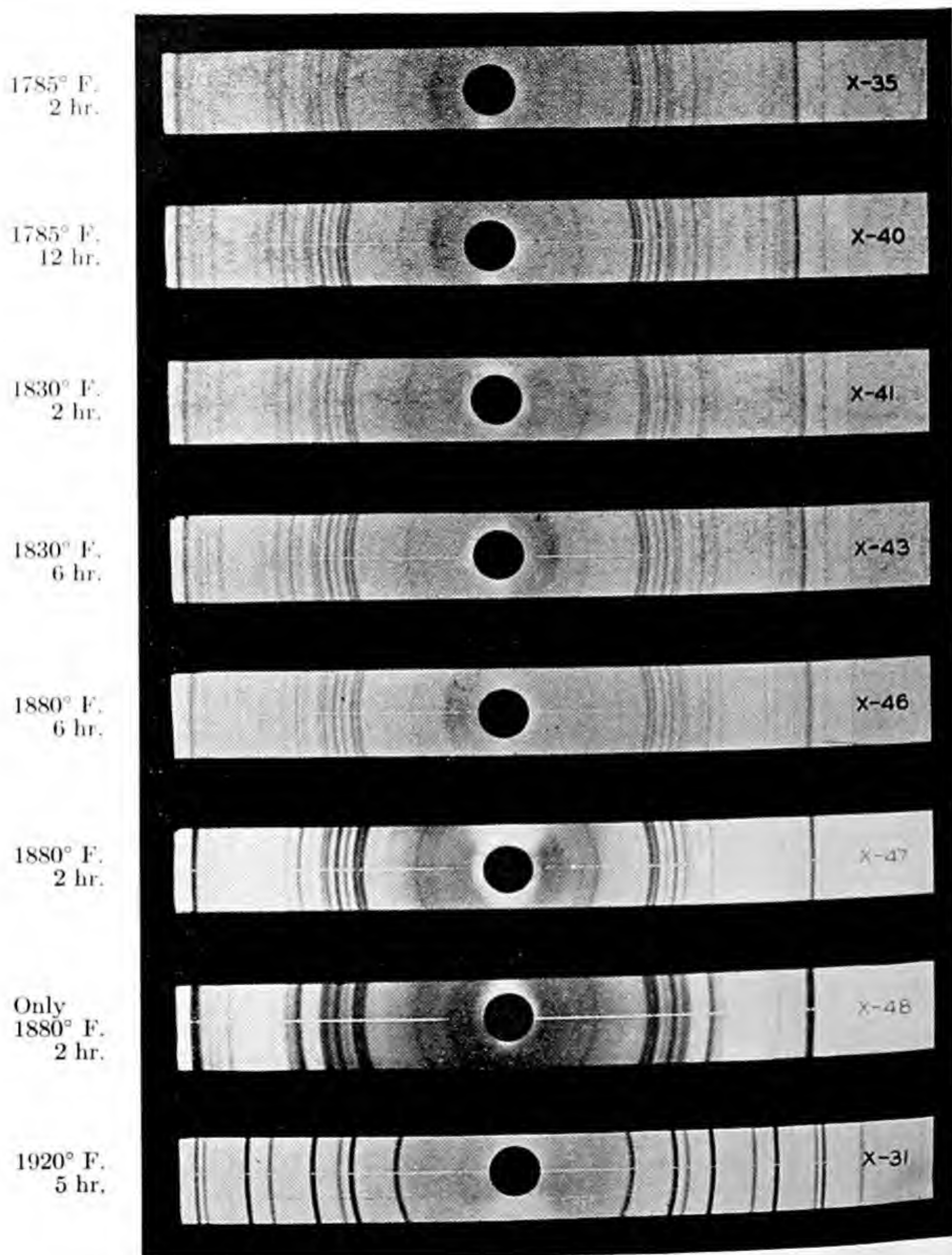


FIG. 21. Debye-Scherrer diagrams of heated alumina gel.

time-consuming, but the presence of the molybdena seemed to make the change of the x-ray patterns an all or nothing effect.

The need for obtaining a more stable alumina catalyst led to the study of gel aluminas and it is with some of these gels that the next discussion will be concerned.

The particular alumina gel to be considered here was prepared from aluminum nitrate which had been precipitated by ammonia and washed. It was then subjected to a few heating tests which quickly revealed that it was far more stable than the low soda alumina. Thereafter, a sample was placed in an electric muffle and small samples removed periodically. When little or no further change in the powder diagrams or the small angle scatter patterns could be noted, the temperature was raised and the heating continued. Thus, each sample had a cumulative heating. Figures 20 and 21 show the powder diagrams of some of the samples, as well as the temperature at which they were heated. The starting sample was nearly amorphous. The heating at 1470°F. for 353 hours produced a distinct change as a comparison of X-4 and X-12 show. After this, a much slower change takes place because X-13 is not far different from X-12 and X-20 just shows a slight sharpening and development of the lines. Raising the temperature to 1650°F. sharpened the diagram considerably but further heating at this temperature was of small effect. The remaining diagrams show the results of heating small samples of essentially X-30, at temperatures varying from 1740 to 1920°F. A most interesting pair among these is X-47 and X-48. They were both heated at 1880°F. for 2 hours but the former had had a preliminary cumulative heating while the latter had had no high temperature treatment prior to the final heating. The effects of the earlier heatings on X-47 are distinctly seen in the sharpness of the lines as contrasted to those of X-48.

The average crystallite sizes of certain of these specimens which showed no detectable trace of corundum were determined from x-ray spectrometer runs on the 1.40 A. line. The crystallite radii run from 42 to 79 A., the sizes increasing with increasing heating temperatures. There appear to be some slight inconsistencies but they are within the limits of the experimental errors. The trend is distinct. Here, too, it is of interest to compare X-47 and X-48. The latter has only increased its crystallite size by 50%, while the crystallites of the former have just about doubled in size.

Small angle x-ray scattering studies were also made on these catalysts and the usual measurements and analyses of the data were made. The results were plotted with the particle size as abscissa and the weight per cent of the particles of this particle size as ordinate and the datum points were connected by a line to yield the simulated distribution curve. (Jellinek, Solomon, and Fankuchen, 18). It is obvious that a wide range of particle

sizes is present, sizes right up to the upper limit that can be reached by the straightforward method of small angle scatter study. This suggested that studies made this way would cover only the part of the specimen composed of particles below a certain limit of size. The two crystal method offers the possibility of raising this limit.

It is useful to determine which part of a given specimen responds to small angle measurements, i.e., whether certain parts of the specimen consist either of particles too large or too small to be studied by this method.

From the theoretical discussion in the first part of this paper, it can be shown that the intercept K 's of successive tangents to the scattering curve (Jellinek, Solomon, and Fankuchen, 18) divided by R^3 (obtained from the slope) give quotients which would be proportional to the weight of the particles of this specific size. If experimental conditions are rigidly controlled so that the same weight of specimen is in the x-ray beam in each experiment, and if, for each sample analyzed, the $\sum_n K_n/R_n^3$ is evaluated, the value of this sum, "M" is proportional to the amount of sample contributing a measurable scattering. If one of the mildly heated samples consisting almost exclusively of very small particles is arbitrarily selected as a base and it is assumed that all its particles have measurable scattering, all other samples can be related to this one. Thus, the "M" value of each sample is divided by the "M" value of the standard and all the weights of the fractions of varying size particles of the sample under consideration are multiplied by this fraction. This has the effect of correcting the weight distribution by a factor determined by the fraction of the sample that consists of particles that have grown too large to be measured by this method.

The results of such small angle analyses on certain alumina gel samples is illustrated in Fig. 22. The solid points are the actual values of radii and weights determined by analysis of small angle scatter. In the upper right corner of each graph is entered the value of "M" for that specimen. The broken lines are the distributions corrected as just described and the arrows are at the points where the average crystallite sizes were determined to be. Therefore, the shapes of these curves give the distribution of those particles which could be measured by small angle scatter and the position of the broken line between the base line and the solid line is an indication of the relative proportion of material that was not measurable. These curves showed that the distributions changed in the sense of indicating the presence of more larger particles and also of more unmeasurable material (because the particle size is too large) as the severity of the heat treatment was increased. The fact that highly heated, or well crystallized specimens of alumina are not suitable samples for small angle scatter measurements

with the standard apparatus is shown by the distribution diagram of sample X-43, where the distribution of the measured particles represented merely about 9% of the total sample.

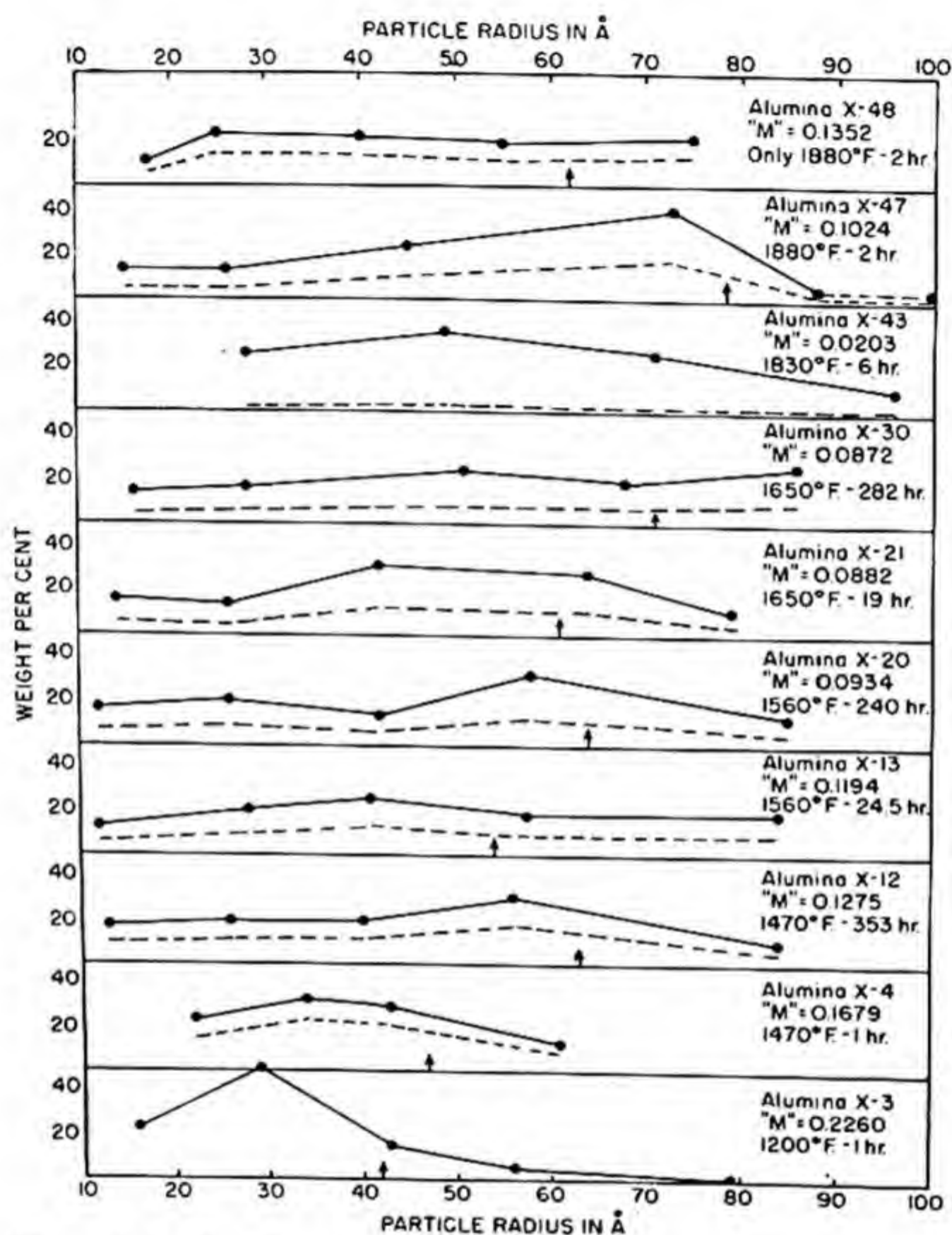


FIG. 22. The weight distributions of particle sizes obtained from small angle scatter from heated alumina gel.

One apparent contradiction must be pointed out. Fig. 22 shows the results of some small angle studies on alumina gels. The arrows indicate the crystallite size as determined from line width measurements. In every case this arrow is at a value of R greater than that corresponding to the peak as determined by the small angle scattering. It would appear that by definition the particle size should always be equal to or larger than the crystallite size.

There are several possible reasons for this discrepancy and it is probable

that all of them are partially responsible. In the first place, the small angle measurements favor the small particles despite the correction factor introduced because this correction does not change the shape of the distribution curve. Secondly, the spectrometer measurements which were used for the crystallite size computation were made continuously without taking individual counts across the diffraction line, and flat, instead of curved, specimens were used. Both of these last two effects cause the line shapes to become somewhat warped and thus introduce errors. Lastly, the very form of the line shape when there is a distribution of crystallite sizes markedly favors large crystallites. The first and last reasons are probably the decisive ones, as they both tend to produce the observed disagreement between the results of both methods.

Silica gel cracking catalysts have also been studied. These materials are amorphous and yield no powder diagrams but they do give a very marked small angle scatter. If the particle distributions obtained from small angle scatter are used to calculate surface areas and these areas are related to the activity, fairly reasonable correlations result. Certain complications concerning these relationships are introduced by various types of treatments applied to the catalysts and by the iron content of commercially deactivated samples.

III. CONCLUSION

Only a small part of the recent x-ray work in catalysis has been discussed here. An important point is that the study of solid catalysts by the method of x-ray scatter touches on many aspects of catalytic research. Especially when used in conjunction with other physical and chemical methods, it has proved a powerful tool over a very wide range of applications, from its use as a control in catalyst production and technical use, to the highly theoretical question as to the mechanism of surface catalysis. We still know much too little about what makes a given solid a catalyst but undoubtedly the answer must to a large extent concern the structural factors involved. X-ray studies will undoubtedly furnish some of the solutions of many as yet unsolved problems.

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Names in parentheses indicate senior authors of the references and are included to assist in locating references where a particular name is not on a given page.

Example: Anderson, J., 33 (see McAllister) means that McAllister *et al.* will be mentioned on page 33, the *et al.* accounting for Anderson. This article can be located under McAllister in the list of references. Numbers in italics refer to the pages on which references are listed in bibliographies at the end of each article.

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